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ACUREX FINAL REPORT FR-80-42/AS

SYNTHESIS OF IMPROVED PHENOLIC AND POLYESTER RESINS

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Acurex Corporation
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Prepared for
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16. Abstract

Thirty-seven addition cured phenolic resin compositions were prepared and tested for their ability to provide improved char residues and moisture resistance over state-of-the-art epoxy resin composite matrices. Cyanate, epoxy novolac and vinyl ester resins were investigated. Char promoter additives were found to increase the anaerobic char yield at 800°C of epoxy novolacs and vinyl esters.

Moisture resistant cyanate and vinyl ester compositions were investigated as composite matrices with Thornel 300 graphite fiber. A cyanate composite matrix provided state-of-the-art composite mechanical properties before and after humidity exposure and an anaerobic char yield of 46 percent at 800°C. The outstanding moisture resistance of the matrix was not completely realized in the composite. Vinyl ester resins showed promise as candidates for improved composite matrix systems.

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SUMMARY

Thirty-seven addition cured phenolic resin compositions were screened for anaerobic char yields at 800°C and moisture resistance. The processing characteristics, cure properties, and heat distortion temperatures of novolac epoxies, novolac cyanates, and unsaturated polyesters were determined. A cyanate resin blend essentially met the project goals to provide state-of-the-art {177°C (350°F) performance} composite mechanical properties before and after humidity exposure, as well as high char yields at 800°C. Composites made with Thornel 300 graphite fiber exhibited state-of-the-art composite properties. The resin matrix had an anaerobic char yield of 46 percent at 800°C and the composite's strength retention after moisture exposure was better than that of state-of-the-art epoxy systems. However, the outstanding moisture resistance of the matrix was not completely realized in the composite. The as-supplied fiber size is suspected to be part of the cause.

Vinyl ester resins showed promise as candidates for an improved composite matrix system. Room temperature flexural strengths of 1585 MPa (230 ksi) and short beam shear strengths of 95.1 MPa (13.8 ksi) were obtained for one system. Char yields as high as 30 percent were obtained on some vinyl ester systems with low concentrations of char promoter additives.

Both the cyanate and vinyl ester Thornel 300 composites showed essentially no strength degradation during exposure to 177°C (350°) in air for 500 hours.

Even though heat distortion temperatures of 250°C (482°F) were demonstrated for resorcinol-formaldehyde novolac cured epoxy resins, the moisture sensitivity of the investigated systems offered no improvement over state-of-the-art systems.

Twenty one char promoting catalysts were investigated for their ability to increase the char yields of the three classes of resin systems investigated. Both epoxy and vinyl ester resins were found to be susceptible to char yield improvements through use of such additives. Low concentrations of phosphorus-nitrogen (PN) additives produced nominal 20 percent increases in the char yields of these systems.

SECTION 1

INTRODUCTION

1.1 Background

The principal objective of the program as conceived was to synthesize high char producing phenolic and polyester resins for use as matrix resins in high performance fiber-reinforced composites. At approximately the mid-point of the program, this objective was modified to include the development of moisture resistant matrix resins while maintaining good char yield.

Commercially available low-cost, intermediate temperature matrix resins used in fiber-reinforced composite applications possess poor resistance to extreme temperature environments. On exposure to fire environments significant loss of the matrix resin results. This can lead to unsupported and exposed fibers. When such unsupported fibers are graphite and they are not consumed in the fire, a potential danger of contaminating the immediate environment with these fibers exists (Reference 1).

One possible approach to minimize this potential danger is to employ matrix resins which produce a high char yield on exposure to fire environments. Polyester and addition cured novolac resins were investigated by Acurex under NASA-Lewis sponsorship for high char yield production and their ability to provide state-of-the-art composite mechanical properties (References 2 and 3).

Concurrent with these previous Acurex efforts were other efforts to determine the actual risk to the environment posed by use of graphite composites in aircraft. Results from these risk assessments (Reference 4)

caused a reevaluation of the original goals of the program and while the fire resistance of graphite composites remains poor, improved fire resistance must be accompanied by environmental durability better than or equivalent to state-of-the-art composite systems.

The strength degradation of graphite composites upon exposure to humid environments is well known and is principally due to water plasticization of the matrix resin. Reduced water absorption characteristics of the matrix resin lead to more moisture durable composites.

1.2 Approach

The three most promising resin systems selected from previous efforts (References 2 and 3) for development of high char producing matrix resins were the novolac oxirane ether, the novolac cyanates and unsaturated polyesters. Briefly, the previous efforts established the following.

Novolac Oxirane Ethers

Novolac (mp 80°C) cured epoxy novolac (DEN 438) in the presence of phosphorus and nitrogen produced an anaerobic char yield at 800°C of 47 percent. This was increased to 59 percent by high temperature air treatment of the resin. Hydroxy aromatic cured oxirane ethers however are known to not produce high HDTs due to the low final crosslink densities obtained.

With four percent of a P-N additive and 1.6 phr catalyst, homopolymerized DEN 438 had acceptable graphite prepreg properties with the exception of its ambient storage life which was approximately one week. Even though graphite fiber (Thornel 300) composites were quite easily fabricated from prepreg due to its low flow characteristics, the DEN 438/Thornel 300 composites demonstrated only marginal strengths at 177°C (350°F). Flexural strength and interlaminar shear strength retention of ambient values at 177°C (350°F) were approximately 50 percent whereas 5208/Thornel 300 provides 80 percent and 60 percent strength retentions, respectively.

Chemical modifications to the novolac oxirane ethers to produce high char yield and higher elevated temperature composite strengths as well as state-of-the-art moisture resistance were investigated on the present program.

Cyanate Resins

This class of resins without additives provides high char yields as do phenolic resins. The novolac cyanate prepolymer prepared from a novolac (mp 80°C) treated with cyanogen bromide provides graphite prepregs with state-of-the-art drape and tack. Flexural strengths of 1420 MPa (206 Ksi) and interlaminar shear strengths of 45.8 MPa (6.7 Ksi) were obtained for Thornel 300 composites of this resin at 204°C (400°F). Cure at 204°C (400°F) of all the cyanate resins tested however did not lead to complete polymerization of the cyanate groups.

With satisfactory composite strengths and char yields demonstrated for this resin system, cure and moisture resistance characteristics of cyanate resins were addressed on the present program.

Unsaturated Polyesters

Reasonably good char yields were obtained from use of aromatic prepolymers in polyester systems even though no liquid comonomer was found which produced char. Use of 9,9-bis(4-hydroxyphenyl)fluorene with aromatic diacids produced aromatic prepolymers which had excellent solubility in a number of liquid monomers. One prepolymer had complete compatability with styrene and this prepolymer cured with 25 percent by weight styrene produced a 40 percent anaerobic char yield at 800°C without additives. Epoxy type processing (vacuum-pressure) of this blend's Thornel 300 prepregs produced composites with unacceptable mechanical properties. Poor fiber wetout was thought to be the source of this problem and use of liquid comonomers with better fiber wetability and a lower vapor pressure than styrene was indicated.

Since a vinyl ester type* of unsaturated polyester (methacrylate derivatized novolac oxirane ether) produced good ambient composite strengths, methacrylate end capped aromatic polyesters such as the 9,9-bis(4-hydroxyphenyl)fluorene-based prepolymer were to be investigated for high char yield and composite properties attainment on the present program.

Resin systems selected for initial graphite composite evaluation were based on the resin performance in screening tests. The resin screening test for char yield was determination of the anaerobic char yield of a cured powdered resin sample at 800°C. Screening tests for moisture resistance were conducted on 6 mm (1/4 inch) resin cubes. Comparison of the dry and 24 hour water boiled properties provided indication of the basic moisture resistance of all the resin systems. Distortion temperature under load (DTUL) described in Appendix A, moisture weight gain, and visual inspection of the resin cubes were conducted on the resin systems.

A resin system from each resin class was originally planned to be selected for composite characterization, however due to the poor moisture resistance of the investigated epoxy resins, two cyanate resin systems and one unsaturated polyester were selected.

Finally, the best two systems were selected for scale-up and larger composite fabrication and characterization.

*Vinyl esters are products of unsaturated acids such as acrylic acid with epoxy resins.

SECTION 2

OBJECTIVE

The objective of this program was to investigate chemical modification of novolac oxirane ethers, cyanates and unsaturated polyesters to provide oligomers which would produce high char yield and good moisture resistance. Additional target requirements for the prepolymers and polymers were:

- State-of-the-art processability (epoxy-like)
- Maximum cure temperature of 204°C (400°F) and a maximum cure pressure of 1.4 MPa (200 psi)
- Low cost
- 177°C (350°F) to 204°C (400°F) performance capability (mechanical and thermal aging)
- Char yield characteristics equivalent to or better than state-of-the-art phenolic resins
- Mechanical properties equal or better than state-of-the-art graphite composite

SECTION 3

RESULTS AND DISCUSSION

Novolac oxirane ethers, cyanates and unsaturated polyesters were investigated for their ability to produce high char yield and moisture resistance.

Since graphite composites from each of the three classes had been previously fabricated, processability was not considered a serious problem and initial resin screening tests consisted of char yield and distortion temperature under load (DTUL) measurements. Char promoting additives were surveyed and several additive classes were found to be beneficial for obtaining higher char yields with the novolac oxirane ethers and the unsaturated polyesters. Near completion of the additive screening efforts moisture resistance testing was initiated.

The discussion given below describes the numerous resin modifications investigated, their synthesis procedures, cure methods and characterization for char yield and moisture resistance. Since resin cost is an important factor in successful resin systems, synthesis procedures and raw material costs weighed heavily in the decisions to evaluate specific modifications.

Initial composite characterization of three resins follows the description of the screening efforts. This is followed by demonstration of the prepregability, processability and fabrication of 20.3 cm x 20.3 cm

(8" x 8") Thornel 300 graphite reinforced composites from the candidate resins selected.

3.1 Char Promoting Additives

Toward the objective of optimizing the char yield of the three candidate resins, prior efforts focused on obtaining high aromatic content in the polymers through use of compounds such as 9,9-bis(4-hydroxyphenyl)fluorene. Such efforts continued during the present program. An equally attractive method to increase char yield is through use of char-yield-promoter catalysts in the resins.

Relatively little information is available on char promoting catalysts per se for the selected resin systems, however a number of publications on fire retardants is readily available. Although fire retardants can reduce the flammability of resins by a number of mechanisms, increasing the char yield of the resin exposed to fire is generally accepted as one mechanism by which some flame retardants operate. It is noted that catalytic char conversion has been reported in some cases to increase the resin's flammability, presumably due to a more rapid evolution of flammable gases during initial fire exposure. Consequently, even though the field of fire retardant chemistry offers great promise for selection of char promotion catalysts, high char yield per se has in general not been sought by investigators in the fire field. Example of the influence fire retardant additives have in the aerobic and anaerobic char yields of cellulosic fabrics is given in Reference 5.

A literature survey for candidate char-yield-promoter catalysts and fire retardants was undertaken and completed. Several classification schemes for fire retardants exist. Tesoro's classification (Reference 6) was selected for screening additives for char yield benefit to each resin system. This classification system is provided in Appendix B.

Table 1 provides Tesoro's classification and the compounds tested in each class with the homopolymerized novolac oxirane ether, DEN 438 and the

TABLE 1. SCREENING RESULTS OF CANDIDATE RESINS FOR CHAR YIELD BENEFIT WITH FLAME RETARDANTS

Tesoro's Class Number[a]	Selected Additives	Anaerobic Char Yield at 800°C, Percent by Weight	
		Novolac Oxirane Ether[b]	Novolac Cyanate
Unmodified	None	24	61
I	NH_4Br	25	--
	$NH_4SO_3NH_2$	32	57
	Phoscheck P30 (Ammonium Polyphosphate)	47	--
II	Sodium Borate	37	62
III	None	--	--
IV	None	--	--
V	Triphenylphosphine	24	59
VI	DE-71	24	--
	$C_2H_2Br_4$	Did not harden	--
	Chlorowax	29	58
VII	Phosgard C-22R	38	--
	FR 633	25	61
VIII	AA 406[c]	45	61
IX	Fe_2O_3	40	--
	Ferrocene	29	--
	DFR 100	29	58

TABLE 1. (Concluded)

Tesoro's Class Number [a]	Selected Additives	Anaerobic Char Yield at 800°C, Percent by Weight	
		Novolac Oxirane Ether[b]	Novolac Cyanate
Oxidizing Agents	$Sb(C_6H_5)_3$	26	61
	MoO_3	36	--
	NH_4BF_4	35	57
	$SbOCl_2$	30	--
	SeO_2 (10 phr)	27	54
	MnO_2 (5 phr)	37	62
	Cr_2O_3 (10 phr)	30	--
	Organic nitro (21 phr) ←	36 (Nitrophenylene diamine)	--

[a] See Appendix B
[b] DEN 438 (Dow) cured with ethyl methylimidazole (EMI)
[c] Hydroquinone adduct of $PNCl_2$ (see Reference 2)

novolac cyanate resins. Several unsaturated polyester structures were tested with the additives found most effective with the DEN 438 and are discussed later. No compounds were tested from Class III since this class of compounds is inappropriate for the present application. Class IV also is inappropriate since the resins did not contain halogen.

Char yield benefits were sought in this study from low concentrations of additives, due to the need to retain maximum resin strength. The additives were incorporated into the resins at no more than 5 phr* except for the last classification (oxidizing agents) which is an Acurex classification. Additives in this classification were added at the indicated loading level prior to cure. Some of the additives did not volatilize during the char testing and char yields of such systems should be adjusted to compensate for this.

Anaerobic char yields at 800^{o}C were determined and are given in Table 1 for the selected additives with DEN 438 and novolac-cyanate resins. The DEN 438 showed significant variation in char yields - ranging to no benefit to a 23 percentage point increase over the unmodified resin which gave a char yield of 24 percent. The char yield of the novolac cyanates showed essentially no benefit from incorporation of any of the additives.

Acidic compounds (Class I) provided essentially no char yield benefit to the novolac oxirane ethers. The benefit of the Phoscheck P30 to the char yield which is in this class can probably be attributed to the presence of phosphorus and nitrogen which is similar to Class VIII shown in Table 1.

Sodium borate (Class II) shows benefit, however this probably is due to boron.

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*phr = Parts per hundred of resin.

The one member of Class V tested did not show char yield benefit. One organic halogen, chlorowax (Class VI) showed slight benefit whereas the DE-71 (pentabromodiphenyl oxide) did not. One phosphorus halogen compound (Class VII), Phosgard C-22R showed a 14 percentage point benefit whereas the second one tested showed no benefit to char yield. The phosphorus-nitrogen compound, AA 406 (Class VIII) showed excellent benefit.

Under the miscellaneous category (Class IX) mixed benefits are seen with the iron-containing additives (Fe_2O_3, ferrocene and DFR 100). Only the Fe_2O_3 shows benefit. This may be due to the oxidizing nature of the Fe_2O_3 rather than the presence of iron per se. Triphenyl antimony shows no benefit, MoO_3 shows benefit. As to whether benefit is obtained from the Mo or an oxidizing effect is unknown. NH_4BF_4 shows benefit probably again due to the presence of boron as seen with the sodium borate. SbOCl shows little benefit.

With the oxidizing agent class, the MnO_2 clearly shows some benefit while SeO_2 and Cr_2O_3 are marginal. It should be noted that in many instances the additives were present as particulates and greater char yield benefit would be expected from a soluble form of that additive. Cure of the novolac oxirane ether with 4-nitro-o-phenylene diamine is considered a positive result.

Phosphorus-nitrogen compounds show the most benefit to char yield. Boron and oxidizing compounds show about equal benefit. One phosphorus halogen compound showed a 14 percent benefit (Class VII) and the remainder of the compounds tested showed little or no benefit at the 5 phr level.

Efforts then focused on the use of the most promising char yield promoter catalysts for the novolac oxirane ethers in polyester resins. Six resin systems were screened for their ability to provide high anaerobic char yields at 800°C.

The unsaturated polyester resins screened were Koppers G.P. polyester resin with styrene, Dow Derakane 470-36 (with styrene content reduced to 10 percent) and two synthesized vinyl esters. One vinyl ester was from the reaction of 9,9-bis(4-glycidyloxyphenyl)fluorene with methacrylic acid and the second from the reaction of phthalic anhydride with glycidyl methacrylate. Both vinyl esters produced clear viscous liquids with thick consistencies. Diphenic acid with glycidyl methacrylate produced a similar prepolymer except for slight haziness. Conditions to simply produce the vinyl ester of naphthalic anhydride were not achieved. The preparation of these vinyl esters is given in the experimental section of this report.

Table 2 provides the anaerobic char yields of the six polyester resins. They were tested neat, with 5 phr of AA 406, 5 phr of Fe_2O_3 and 5 phr of MnO_2. Included in the table are decomposition temperatures (Td) of the resin systems showing their basic stability as well as the influence of a specific additive has on lowering the decomposition temperature of the resin system.

Anaerobic char yields of the unmodified polyester systems are seen to range from 2-to-16 percent at 800°C. The unmodified resins show char yields consistent with their calculated aromatic and total carbon atom contents, but this does not hold for the resins with additives. Additives show mixed benefits to char yield. In almost all cases, vinyl ester resins with 5 phr of the AA 406 additive show the highest or nearly the highest char yields. It is noted that the AA 406 is not soluble to any great extent in any of these resins. Both oxidizing agent additives (added at 5 phr) provide char yield benefits at 800°C. For instance, methacrylate of the 9,9-bis(4-glycidyloxyphenyl)fluorene with the AA 406 gave a 21 percent char yield and with the Fe_2O_3, a 25 percent char yield, however this includes a ∿5 percent iron residue. The effect on char yield of using the additives, AA 406

TABLE 2. EFFECT OF ADDITIVES ON ANAEROBIC CHAR YIELD OF UNSATURATED POLYESTER RESINS.

Number	Resin (Notebook Reference)	Percent Total Carbon	Percent Aromatic Carbon	Additive									
				None		AA 406[a]		Fe_2O_3[a]		MnO_2[a]		AA 406[a] & Fe_2O_3[a]	
				Td, °C	Yc,[b] %	Td, °C	Yc,[b] %	Td, °C	Yc,[b] %	Td, °C	Yc,[b] %	Td, °C	Yc,[b] %
1	Koppers G.P. Polyester Resin with styrene[c]	Unknown		385	5	357	12	357	10	360	9		
1A	Repeat of 1[c]			345	3							345	14
2	Derakane 470 (10 percent styrene) (32-131)[c]	67.7	29.0	382	9	375	27	362	20	375	21		
2A	Derakane 490 (19 percent styrene) Repeat of 2[c]			375	14							355	26
3	9,9-Bis(4-glycidyloxyphenyl) fluorene with methacrylic acid (50-55)[c]	73.8	47.3	382	16	375	21	340	25	355	23		
3A	Repeat of 3[c]			365	16							330	24
4	Phthalic anhydride with glycidyl methacrylate (50-60)[c]	58.7	16.0	350	2	334	23	341	8	335	10		
4A	Repeat of 4[c]			335	3								
5	2,7-Diglycidyloxynaphthalene with methacrylic acid (50-103)[c]	66.7	30.8	355	13	355	22	315	22				
6	Diphenic acid with glycidyl methacrylate (50-99)[c]	67.0	30.9	365	3	365	12	365	10	370	12	365	13

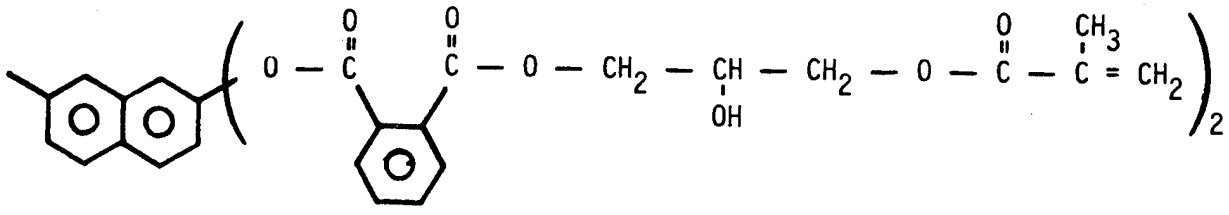
[a] 4 phr Additive in resin
[b] Td = decomposition temperature (knee); Yc = char yield at 800°C in nitrogen (15°C/minute, 0.1 liter/minute, -60 mesh)
[c] Sample cured with 2 phr t-butyl perbenzoate. Cure cycle: RT to 177°C (350°F), 1 hour at 177°C (350°F)

and Fe_2O_3 together, show that the char yield benefits are not additive. That is, the char yields from the resins containing both additives were not significantly higher than the char yields obtained from the resin containing the AA 406 additive alone.

The decomposition temperatures show that the basic thermal stability of the resins was essentially unaffected by the presence of additives.

Since the previously investigated styrene compatible polyester provided a char yield of 43 percent (Reference 3) and the acrylate derivative of DEN 438 provided a 47 percent char yield with 20 percent by weight AA 406 additive (Reference 2), question arises as to what maximum char yields might be expected from the fully optimized vinyl esters in view of the char yields obtained on the models in Table 2. The char yields obtained from both the 9,9-bis(4-glycidyloxy)fluorene and diphenic acid based vinyl ester are poor in view of their starting carbon atom contents. Char retention of the carbon atoms in the DEN 438, phthalic anhydride and 2,7-diglycidyloxy-naphthalene-based vinyl esters was much better in view of their starting carbon atom contents.

Synthesis of a prepolymer such as shown below, improves the aromatic carbon atom content. However, if char efficiencies suggested by the carbon loss results shown in Table 2 hold for such polymers, only minor improvement in char yields can be expected.



Hypothetical new prepolymer with aromatic carbon atom content of 33.9 percent.

Consideration of new monomers and prepolymers must also take into account the following:

- The previous polyester (Reference 3) did not provide high short beam shear strengths

- Acrylate vinyl esters even though they appear to provide higher char yield resins are more sensitive to moisture than the methacrylate vinyl esters (Reference 7).

The char promotion additive efforts for the three resin classes leads to the following conclusions relevant to program goals.

1. Even at low concentrations of several additives significant char yield benefits are obtained with the homopolymerized DEN 438 and unsaturated polyesters. Char yields of the novolac cyanates are not significantly affected by char promoting additives.

2. Phosphorous-nitrogen compounds hold the most immediate promise of obtaining good char yields with the novolac oxirane ethers and the vinyl ester type unsaturated polyesters.

3. Resin structure, additive concentration and selection, and char chemistry appear to be interrelated. Consequently, selection of the optimum char promoting catalyst(s) and its optimum concentration(s) will be the result of a parametric study which includes simultaneous investigation

of other resin parameters such as moisture resistance and/or composite shear properties.

Therefore, under the discussion of the specific resin candidates below due to program budget constraints, even though char yield is documented for each resin composition, char yield optimization per se was not undertaken. Moisture resistance tests were the principal basis for selection of one candidate over another. After attainment of good graphite composite properties, char yield could then be optimized.

3.2 Novolac Oxirane Ethers

Based on the previous efforts with both the homopolymerized DEN 438 and the novolac cured DEN 438 where 177°C (350°F) composite strengths were found to be inadequate, present efforts focused on maximizing the DTUL of hydroxy aromatic cured DEN 438. As discussed below, even though a dry DTUL of 250°C was obtained suggesting improved 177°C (350°F) composite strengths over those obtained on the previous program, the system's moisture resistance probably offers no improvement over current epoxy systems (except for improved char yield).

Investigations focused on hydroxy aromatic cured DEN 438 since an anaerobic char yield at 800°C of 33 percent was obtained with a novolac cured DEN 438 on the previous effort. With 17 phr of AA 406 the char yield of this composition was increased to 47 percent. Its DTUL however, was only 150°C. Specifically higher melting novolacs such as obtained from naphthol with formaldehyde or novolacs which would increase the final crosslink density such as rescorcinol with formaldehyde were investigated. Novolacs were prepared by condensation procedures given in Sorenson and Campbell using oxalic acid as a catalyst (Reference 8).

Table 3 gives the results of the 24 hour water boil resistance and char yield testing the several epoxy compositions investigated. MY 720, the

TABLE 3. MOISTURE RESISTANCE AND CHAR YIELD CHARACTERIZATION OF NOVOLAC CURED EPOXY RESINS[a]

Code	Resin Components (Parts by Weight)	DTUL, °C @ 3.1 MPa (449 psi) and 15°C/minute Heating Rate[b]			Weight Change with Water Boil and Redry			Y_c[c] (Percent)
		Initial	24 Hr Water Boil	Δ Tg	Percent Weight Gain Water Boil	% Wt Gain After Redry 1 Hr @ 220°C	Cracks in Sample After Redry	
C-41	DEN 438 (53)/naphthol-formaldehyde novolac (47)/BDMA (1)	175	118	-57	8.58?	-1.06	No	30
C-42	DEN 438 (51)/naphthol-formaldehyde novolac (44)/AA 406 (5)/BDMA (1)	175	148	-27	3.98	-0.92	↓	35
C-45	MY 720 (41)/naphthol-formaldehyde novolac (59)	193	158	-35	3.66	-1.42		32
C-49	MY 720 (66)/resorcinol-formaldehyde novolac (33)	(250)	108	-142	4.09	-1.32		33
C-50	MY 720 (32)/0510 (32)/resorcinol-formaldehyde novolac (34)	(240)	110	-130	4.79	-0.75		36
C-51	MY 720 (59)/2,4-dihydroxynaphthalene-formaldehyde novolac (41) (heterogeneous)	(207)	(155)	-52	4.06	-1.16		28
C-52	MY 720 (28)/0510 (28)/2,7-dihydroxynaphthalene-formaldehyde novolac (40) (heterogeneous)	170, (215)	188, (142)	-52, -73	3.35	-0.30	↓	27

[a]Cure schedule: held at 87°C until gelled, then cured through one hour at 157°C and four hours at 204°C
[b]Parenthesis indicate expansion Tg without penetration
[c]Char yield at 800°C in N_2 (0.2 liter/minute) at a heating rate of 15°C/minute; sample through 60 mesh

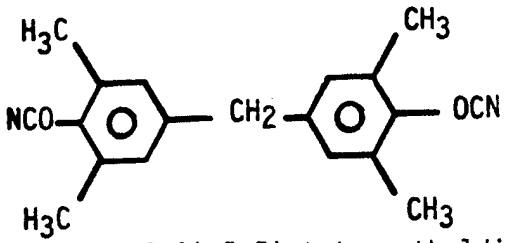
tetraglycidyl adduct of methylene dianiline, was included in the investigation for its ability to provide high crosslink densities. Compositions C-41 (DEN 438) and C-45 (MY 720) show that with the naphthol formaldehyde novolac curative a higher DTUL is obtained with MY 720 than with DEN 438. The BDMA catalyst required for DEN 438 was not found to be required to cure the MY 720 composition probably due to the glycidyl amine structure in the MY 720. Using the resorcinol-formaldehyde novolac as a curative for MY 720, a DTUL of 250^{o}C was obtained. This is equivalent to the DTUL obtained from diaminodiphenyl sulfone cure of MY 720 (Reference 9). Even though this system provided a char yield of 33 percent without additives, it underwent severe DTUL loss upon 24 hour water boil as well as moisture weight gains equivalent to state-of-the-art systems (Reference 9).

Efforts with similar systems to reduce their moisture sensitivity would probably require use of MY 720 for its obvious ability to provide high HDTs and highly functional curatives such as the resorcinol-formaldehyde novolac. Methyl resorcinol or other suitably derivatized dihydroxy benzenes condensed with formaldehyde or fluorenone would be expected to lead to novolacs which would lead to MY 720 systems with reduced moisture sensitivity.

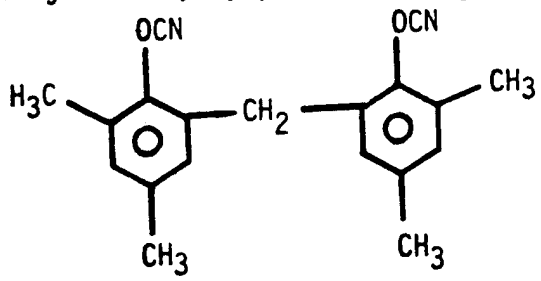
Further efforts with oxirane ether systems were not carried out due to more promising results obtained simultaneously with the cyanate resin systems which are discussed below.

3.3 Novolac Cyanate Resins

Efforts on the cyanate resins started with synthesis and characterization of the two monomers shown below. Synthesis procedures are given in the experimental section of this report.



4,4'-Dicyanato-3,3',5,5'-tetramethyldiphenylmethane(4,4'-DCTMDM)



2,2'-Dicyanato-3,3',5,5'-tetramethyldiphenylmethane(2,2'-DCTMDM)

From the characterization and comparison to the previously characterized novolac cyanate (Reference 3), chemical modifications were carried out as discussed below to improve the moisture resistance, DTULs and/or char yields of cyanate resin systems.

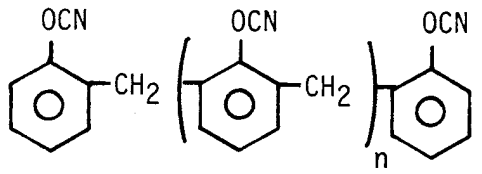
For a one-to-one comparison of the new monomers to the previously characterized novolac-cyanate, a new batch of the novolac cyanate was synthesized. Gel times of the pure monomers were in excess of two hours at 125°C however, use of 0.5 phr zinc stearate reduced the gel times to less than 15 minutes at 125°C. Char yield and DTUL investigations (dry and after 24 hour water boil) for the three cyanate resins are given in Table 4. An idealized structure of the novolac cyanate is also provided in Table 4.

The polymerized cyanate monomers exhibited good 24 hour water boil resistance and thermal properties. The 4,4'-DCTMDM resin gave DTULs about 50°C higher than the 2,2'-DCTMDM resin. Neither system, however, provided the unusually high DTULs obtained on the baseline novolac cyanate resin. Average DTUL values obtained on the three resin systems were as follows:

TABLE 4. NEAT RESIN PROPERTIES OF INITIAL CYANATE RESINS

Code	Polymers[a]	Catalyst[b] System		DTUL, °C at 449 psi and 15°C/min Heat Rise: Initial	DTUL: 24 hr Water Boil	DTUL: ΔTg	Weight Change With Water Boil and Redry: % Wt Gain 24 hr Water Boil	% Wt[d] Gain after Redry (1 hr at 200°C)	Cracks in Sample After Redry	Y_C[c] Percent
C-14	Baseline novolac cyanate	A	As prepared	330	230	- 100	4.36	1.30	N	55
C-12	2,2'-Dicyanato-3,3',5,5'-tetramethyl Diphenylmethane (2,2'-DCTMDM)	A	As prepared	160	145	- 15	5.31	-0.90	N	28
		A	As prepared	160	158	- 2	2.38	0.00	N	28
C-28	2,2'-DCTMDM	B	Recrystallized	165	155	- 10	0.91	-0.08	Y	27
C-13	4,4'-Dicyanato-3,3',5,5'-tetramethyl Diphenylmethane (4,4'-DCTMDM)	A	As prepared	170	160	- 10	0.50	-0.50	N	31
C-15	4,4'-DCTMDM (second preparation)	B	As prepared	216	195	- 21	1.78	0.12	Y	32
C-11	4,4'-DCTMDM	B	Recrystallized	219	209	- 10	1.01	0.23	N	31
C-26	4,4'-DCTMDM (second preparation	B	Recrystallized	206	198	- 8	1.10	0.19	N	34

[a] Heated at 125°C until gelled, then cured through one hour at 204°C
[b] A: 5 phr of 10 percent zinc stearate in completely trimerized 2,4-dimethylphenyl cyanate
B: 5 phr of 10 percent zinc stearate in partially trimerized 2,4-dimethylphenyl cyanate
[c] Char yield at 800°C in N_2 (0.2 liter/minute) at a heating rate of 15°C/minute: sample through 60 mesh
[d] Weight gains shown for the samples indicate that the original sample weight was not obtained (redry incomplete or water chemically reacted with polymer)



Idealized structure of novolac cyanate

Resin System	DTUL, ^{o}C
Novolac cyanate	330
2,2'-DCTMDM	162
4,4'-DCTMDM	214

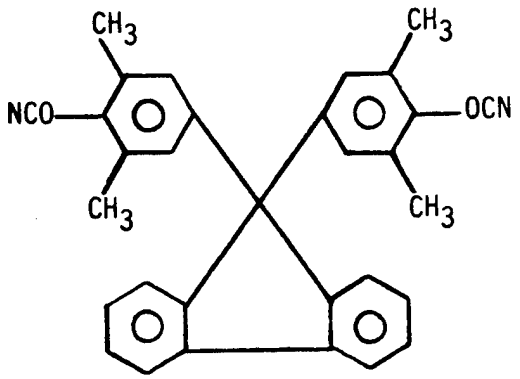
Complete reaction of the cyanate functionality occurred at the 204^{o}C cure temperature (DSC, IR spectra) in the diphenylmethane-based cyanates whereas the novolac-cyanate resin showed residual cyanate functionality after initial cure at 204^{o}C. Continued cure (24 hours) of the novolac cyanate at 204^{o}C however, resulted in complete loss of the cyanate functionality and appearance of isocyanurate by IR spectral analysis in the presence of the zinc catalyst.

The moisture resistance of the DCTMDM polymers as determined by DTUL after 24 hour water boil was excellent. An average DTUL loss of only 11^{o}C (shown as Δ Tg in the table) was obtained on these polymers compared to a 100^{o}C loss on the novolac-cyanate after 24 hour water boil. The as-prepared 2,2'-DCTMDM polymer showed high moisture weight gains after water boil (with little loss in DTUL) whereas 2,2'-DCTMDM polymer resulting from crystallized monomer showed only a nominal one percent weight gain due to 24 hour water boil. This may be due to impurities in the as-prepared resin. The 4,4'-DCTMDM polymer showed only modest moisture weight gains after 24 hour water boil in both the as-prepared and crystallized monomers. The 4,4'-DCTMDM prepolymer was selected for continued efforts due to its higher DTUL.

The properties of the polymerized cyanate monomers are also dependent on the catalyst and heat schedule utilized in the polymerization process. When neat zinc stearate at 0.5 phr was used as the cure catalyst, its solubility rate was slow in the melted monomers at 125^{o}C, causing initial gelation around the undissolved particles. Ten percent zinc stearate was then dissolved in 2,4-dimethylphenyl cyanate (DMPC) by heating slowly to 100^{o}C. This catalyst system was readily soluble in the multifunctional cyanate monomers at 125^{o}C and was added at 5 phr. Zinc stearate was selected for use from Reference 10.

Catalyst system B (Table 4) produced higher DTULs than catalyst system A with the 2,2'-DCTMDM and 4,4'-DCTMDM monomers. This is attributed to the copolymerization of the DMPC with the dicyanate monomers, whereas, in catalyst system A, the DMPC is nearly completely polymerized (IR spectra) prior to its addition to dicyanate monomers. Apparently with catalyst system A, the tris(2,4-dimethylphenoxy)triazine acts as a plasticizer in the resin whereas with system B the 2,4-dimethylphenyl cyanate reacts into the forming polymer network.

9,9-Bis(3,5-dimethyl-4-cyanatophenyl)fluorene (structure below) was synthesized and its polymerization attempted both neat and with 30 mole percent 2,4-dimethylphenyl cyanate. No catalyst was used.

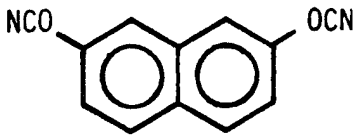


9,9-Bis(3,5-dimethyl-4-cyanatophenyl)fluorene

This monomer's high crystallinity (compared to the 9,9-bis(4-cyanatophenyl)fluorene) disallows its ready solubility in either the previously described diphenyl methane based monomers or the 2,4-dimethylphenyl cyanate. Only heterogeneous systems (undissolved 9,9'-bis(3,5-dimethyl-4-cyanatophenyl) fluorene) were obtained. Efforts with this monomer were discontinued.

Anaerobic char yields at 800^{o}C of the 2,2'-DCTMDM and 4,4'-DCTMDM polymers averaged 31 percent. This represented a loss of 20 percentage points in char yield from the novolac cyanate resin.

Efforts then focused on the use of reactive diluents to increase the char yield of the moisture resistant 4,4'-DCTMDM resin system and increase the moisture resistance of the high char yield 2,7-dicyanatonaphthalene resin system (structure below).



2,7-Dicyanatonaphthalene(2,7-DCN)

Accordingly, the monofunctional compounds, 4-phenylphenyl cyanate, 1-naphthalene cyanate, and 2,4-dimethylphenyl cyanate were synthesized and copolymerized with the 4,4'-DCTMDM and 2,7-DCN monomers.

Table 5 gives the results of moisture resistance and char yield testing of these systems. The unmodified 4,4'-DCTMDM and 2,7-DCN resins are included for comparative purposes. No significant improvement in the char yield of the 4,4'-DCTMDM resin was obtained by use of either the 4-phenylphenyl cyanate or 1-cyanatonaphthalene. When the 2,7-DCN was copolymerized with the 4,4'-DCTMDM, improvements in char yields (31-to-42) and DTULs (219-to-230) were observed. A slight decrease in moisture resistance was observed and as discussed below is due to the moisture sensitivity of the 2,7-DCN resin. The 4,4'-DCTMDM resin with 5 phr of the char promoting additive, AA 406 resulted in only a three percent char yield improvement (31-to-34).

Use of the monofunctional cyanates with the 2,7-DCN resin resulted in improved moisture resistance but lower char yields. The unmodified 2,7-DCN resin has residual cyanate groups from incomplete polymerization

TABLE 5. MOISTURE RESISTANCE AND CHAR YIELD CHARACTERIZATION OF MODIFIED CYANATE RESINS

Code	Polymers and Additives[a]	Catalyst[b] System	DTUL, °C at 3.1 MPa (449 psi) and 15°C/minute Heating Rate			Weight Change With Water Boil and Redry			Y_c (c) (Percent)
			Initial	24 Hr Water Boil	ΔTg	% Wt Gain Water Boil	% Wt Gain[d] After Redry 1 Hr @ 200°C	Cracks in Sample After Redry	
C-11	4,4'-Dicyanato-3,3',5,5'-tetramethyl diphenylmethane (4,4'-DCTMDM)	B	219	209	-10	1.01	0.23	N	31
C-7	4,4'-DCTMDM plus 30 phr 4-phenylphenyl cyanate	A	131	137	+6	1.03	-0.45	N	30
C-8	4,4'-DCTMDM plus 30 phr 1-cyanatonaphthalene	A	123	126	+3	1.13	-0.61	N	28
C-27	4,4'-DCTMDM plus 30 phr 2,7-Dicyanatonaphthalene	B	238	214	-24	1.40	0.35	N	42
C-37	2,7-Dicyanatonaphthalene (2,7-DCN)	None	267	195	-72	1.78	0.85	Blistered	64
C-9	2,7-DCN plus 30 mole percent 2,4-dimethylphenyl cyanate	None	246	208	-38	2.02	1.13	Slight Blistering	57
C-35	2,7-DCN plus 30 mole percent 1-cyanatonaphthalene	None	234	202	-32	0.93	0.21	Slight Blistering	53
C-36	2,7-DCN plus 30 mole percent 4-phenylphenyl cyanate	None	246	212	-34	1.17	0.46	Slight Blistering	49

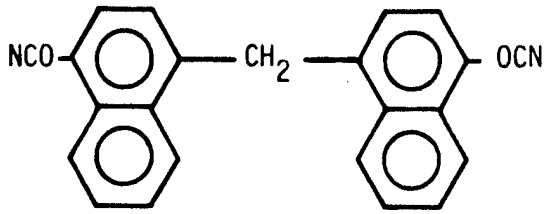
[a] Heated at 125°C until gelled, then cured through one hour at 204°C (400°F)
[b] A: 5 phr of 10 percent zinc stearate in nearly completely trimerized 2,4-dimethylphenyl cyanate
B: 5 phr of 10 percent zinc stearate in partially trimerized 2,4-dimethylphenyl cyanate
[c] Char yield at 800°C in N_2 (0.2 liter/minute) at a heating rate of 15°C/minute; sample through 60 mesh
[d] Positive weight gains shown for the samples indicate that the original sample weight was not obtained (redry incomplete or water chemically reacted with polymer)

at 204°C (400°F) which may be related to the severe blistering observed with the water boiled specimens upon redry. The modified 2,7-DCN systems have lower DTUL's suggesting that more complete polymerization could occur. Even though the blistering was reduced in the modified resin, it was not eliminated. This behavior was unacceptable for program purposes. The modified 2,7-DCN resins do show improved moisture resistance as indicated by DTUL shift due to 24 hour water boil.

The influence that the monofunctional modifiers have on the char yield of the 2,7-DCN system is interesting. The unmodified 2,7-DCN system has a char yield of 64 percent while the 1-cyanatonaphthalene and 4-phenylphenyl cyanate modifications have char yields of 53 and 49 percent respectively. All three systems are completely "aromatic" and yet show significant differences in char yields.

At this juncture a Thornel 300 graphite composite was prepared to ascertain the high temperature (177°C) properties of the 4,4'-DCTMDM system. A Thornel 300 graphite composite was fabricated and tested (see Section 3.4). It showed only a 70 percent short beam shear strength retention at 250°F after 24 hour water boil. Essentially no useful 177°C (350°F) short beam shear strength was retained after 24 hour water boil. Since the DTUL of the 24 hour water boiled resin was only 198°C (388°F), a higher "wet" Tg resin was needed to give useful 177°C (350°F) strengths after moisture exposure.

Consequently, a novolac resin prepared from 1-naphthol and formaldehyde was treated with cyanogen bromide. The naphthol novolac cyanate monomer is sketched below. 2,4-Dimethylphenyl cyanate and 1-naphthol cyanate were investigated as reactive diluents for the resin system for possible benefits to cure completion at 204°C (400°F) and enhanced moisture resistance. The char yields of the systems were also determined.



Cyanate monomer from 1-naphthol condensed with formaldehyde (mixed isomers?)

Table 6 gives the results of the moisture resistance and char yield testing on the naphthol novolac cyanate resin system. Even though a very high initial DTUL of 291°C was obtained on the dry system, the Tg shift due to 24 hour water boil was high (69°C) and its moisture weight gain excessive. Addition of 25 phr 2,4-dimethylphenyl cyanate and 1-cyanato-naphthalene reduced the Tg shifts to 25°C and 43°C respectively, as well as reduced the weight gains experienced with water boil. The final wet Tgs of these later two systems are approximately the same as the 4,4'-DCTMDM system (wet) and no benefit from use of these systems is seen with a possible exception of their char yields which ranged from 42-to-52 percent.

As subsequently discussed in Section 3.5, with crystallization of the 4,4'-DCTMDM monomer from a mixture of cyclohexane and hexane (in combination with higher cure temperature) increased wet and dry DTULs were obtained and modest composite strengths were obtained at 177°C (350°F). These strengths however were not as high as those obtained from novolac cyanate resin composites. The 177°C (350°F) short beam shear percent strength retention of the 4,4'-DCTMDM composite after 24 hour water boil however was better than the novolac cyanate composites.

Blends of the 4,4'-DCTMDM with the 2,7-dicyanato naphthalene and novolac cyanate resins were surveyed for selection of a composite resin candidate with higher initial short beam shear strengths at 177°C (350°F) than the 4,4'-DCTMDM system. Table 7 gives the results of the moisture resistance and char yield testing of these blends. System C-63 (50 percent weight 4,4'-DCTMDM/50 percent weight phenol-formaldehyde novolac cyanate) was chosen for Task II efforts due to the ease of obtaining a suitable liquid B staged prepolymer for graphite prepreg formation. The char yield and

TABLE 6. MOISTURE RESISTANCE AND CHAR YIELD CHARACTERIZATION OF NAPHTHOL NOVOLAC CYANATE RESIN

Code	Polymers and Additives[a]	Catalyst[b] System	DTUL, °C at 3.1 MPa (449 psi) and 15°C/minute Heating Rate			Weight Change with Water Boil and Redry			Y_c[c] (Percent)
			Initial	24 Hr. Water Boil	Δ Tg	% Wt. Gain Water Boil	% Wt. Gain After Redry 1 Hr. @ 200°C	Cracks in Sample After Redry	
C-40	Naphthol novolac cyanate	None	291	222	-69	3.26	-0.61	N	52
C-43	Naphthol novolac cyanate with 25 phr 2,4-dimethylphenyl cyanate	B	211	186	-25	1.33	-0.40	N	47
C-44	Naphthol novolac cyanate with 25 phr 1-cyanatonaphthalene	B	238	195	-43	1.81	-0.79	N	42

[a]Heated at 106°C until gelled, then cured through one hour each at 156°C, 204°C, and 228°C
[b]B: 5 phr of 10 percent zinc stearate in partially trimerized 2,4-dimethylphenyl cyanate
[c]Char yield at 800°C in N_2 (0.2 liter/minute) at a heating rate of 15°C/minute; sample through 60 mesh

TABLE 7. MOISTURE RESISTANCE AND CHAR YIELD CHARACTERIZATION OF CYANATE RESIN BLENDS[a]

Code	Resin Components (Parts by Weight)	Catalyst[b]	DTUL, °C @ 3.1 MPa (449 psi) and 15°C/minute Heating Rate			Weight Change with Water Boil and Redry			Y_c[c] (Percent)
			Initial	24 Hour Water Boil	Δ Tg	% Weight Gain 24 Hour Water Boil	% Wt. Gain After Redry 1 Hr @ 200°C	Cracks in Sample	
C-27	4,4'-DCTMDM (77)/2,7-dicyanatonaphthalene (23)	Y	238	214	-24	1.40	0.35	N	42
C-61	4,4'-DCTMDM (50)/2,7-dicyanatonaphthalene (50)	N	227	210	-17	1.81	0.36	N	41
C-62	4,4'-DCTMDM (70)/baseline novolac cyanate (30)	Y	218	200	-18	2.12	0.40	N	42
C-63	4,4'-DCTMDM (50)/baseline novolac cyanate (50)	Y	250	225	-25	1.90	0.46	N	46

[a]Cure schedule: 2 hours at 121°C (250°F), one hour at 166°C (330°F), four hours at 218°C (425°F)
[b]5 phr of 10 percent zinc stearate in partially trimerized 2,4-dimethylphenyl cyanate
[c]Char yield at 800°C in N_2 (0.2 liter/minute) at a heating rate of 15°C/minute; sample through 60 mesh

moisture resistance of all the blends are seen in Table 7 to be nearly equivalent.

Further discussion of the cyanate resin systems and rationale for selection of candidates for composite evaluation is given in Section 3.4.

3.4 Unsaturated Polyesters

Principally based on the attainment of a 93.3 MPa (13,540 psi) short beam shear strength with Dow's Derakane 470-36 (Reference 2), the vinyl ester type of unsaturated polyester, (acrylate and methacrylate derivatives of epoxy resins) were investigated exclusively on the present program. The DTULs of available vinyl esters are too low for 177°C (350°F) performance. It should be noted however, that styrene is used extensively with these systems on an industrial basis for improved economics and further impart good environmental resistance. However, high temperature performance can be effected by the styrene content of such systems.

Table 8 gives the dry and 24 hour water boiled DTULs and char yields of 10 vinyl ester resin systems selected for initial property evaluation. Synthesis procedures are given in the experimental section. Acrylate and methacrylate derivatives of resorcinol diglycidyl ether (RDGE) and DEN 438 were studied principally for the relative contribution each acid had to the moisture resistance and DTULs of their respective vinyl esters. Without styrene as a comonomer for these systems, they were found to be moisture sensitive. RDGE systems are much more moisture sensitive than the DEN 438 systems. In regards to obtaining high initial dry DTULs, methacrylate based vinyl esters provide a 30°-to-40°C benefit over acrylate based systems. (Samples C-18 versus C-16, and Samples C-21 versus C-24). Tg loss due to 24 hour water boil however shows no benefit from use of either acid. DTUL data are somewhat erratic and this may in part be due to varying degrees of polymerization in the samples (even though vinyl group disappearance by infrared examination of the cured resins was indicated).

TABLE 8. RESIN PROPERTIES OF CROSSLINKED ACRYLATE AND METHACRYLATE SYSTEMS

Code	Vinyl Esters Systems	DTUL, °C at 449 psi[a] and 15°C/min			Weight Change with Water Boil and Redry			Y_C^b (%)	Hardness, Barcol
		Initial	24 Hr Water Boil	ΔTg	% Wt Gain 24 Hr Water Boil	% Wt Gain After Redry (1 hr @ 200°C)	Cracks in Sample After Redry		
C-18	RDGE with acrylic acid[c]	83	65	-18	6.4	0.57	Y	15	42
C-19	RDGE with acrylic acid and AA 406 (5 phr)[c]	91	58	-33	6.3	1.20	Y	31	42
C-16	RDGE with methacrylic acid[c]	125	67	-58	5.4	0.66	Y	10	55
C-17	RDGE with methacrylic acid and AA 406 (5 phr)[c]	121	(128)	-7	4.9	1.20	Y	21	52
C-29	Repeat of C-16[c]	(138)	107	-31	4.4	0.07	Y	10	50
C-30	Repeat of C-17[c]	(125)	(122)	-3	4.9	1.50	Y	26	42
C-21	DEN 438 with acrylic acid[c]	(160)	(123)	-37	2.3	0.24	Y	25	40
C-22	DEN 438 with acrylic acid and AA 406 (5 phr)[d]	--	--	--	---	---	-	--	--
C-24	DEN 438 with methacrylic acid[c]	(193)	(133)	-60	2.9	0.42	Y	21	48
C-25	DEN 438 with methacrylic acid and AA 406[c] (5 phr)	125 (177)	(115)	-10; -62	4.0	0.39	Y	26	38
C-31	Derakane 470 (10 percent styrene)[e]	127	111	-16	2.1	-1.50	Y	27	47
C-32	Phthalic anhydride with glycidyl[e] methacrylate	93	50	-43	5.8	----	Y	23	48
C-33	9,9-Bis(4-glycidyloxyphenyl)fluorene[c]	128	130	+2	2.9	-3.12	Y[f]	25	45
	2,7-Diglycidyloxynaphthalene with	133	---	--	----	----	-	22	--
C-34	Diphenic acid with glycidyl[c]	(77)	65	-12	7.3	-3.53	Y	12	55

[a] Parenthesis indicate expansion Tg without penetration
[b] Char yield at 800°C in N_2 (0.2 liter/minute) at heating rate of 15°C/minute; sample through 60 mesh
[c] 0.5 phr T-butylperbenzoate +0.75 phr cumene hydroperoxide catalysts; all cured through one hour at 200°C in air
[d] Sample gelled when milled - no data
[e] Sample cured with 2 phr t-butylperbenzoate. Cure cycle: RT to 177°C (350°F), one hour at 177°C (350°F)
[f] The cured sample contained cracks before 24 hour water boil and redry

The "DEN 438 with methacrylic acid" sample is included in the table for comparison to the commercially available Derakane resin with styrene. Comparison of these two samples (C-24 and C-31) show the influence of the small quantity of styrene has on both initial DTUL and Tg shift due to 24 hour water boil.

Basically, all of the vinyl esters show moisture sensitivity in excess of the previously discussed cyanate monomer, 4,4'-DCTMDM. The Derakane resin appears to be one of the better vinyl ester resins based on char yield and moisture resistance testing.

The following items are concluded from the results presented in Table 8.

1. A 177^{o}C (350^{o}F) performing composite matrix resin is not indicated from DTUL measurements on dry resin cubes.

2. The moisture resistance of the cured systems based on 24 hour water boil tests show moisture weight gains of 2-to-7 percent which are about the values expected for epoxy resins. The Tg shifts based on dry and wet DTUL measurements ranged from a 7^{o}C gain to a 60^{o}C loss which is less than expected for epoxy resins. All systems cracked upon drying at 149^{o}C after 24 hour water boil.

3. Good char yields appear limited (even with char promoter catalysts) by the nature of resin systems. The glycidyl ether portion of the epoxy precursor in combination with the acrylate or methacrylate portion leads to relatively high calculated aliphatic contents in the cured resins. If significant aromatic contents are introduced into the resins, their good processability would be compromised.

Based on the above considerations and the good short beam shear strength obtained previously with the Derakane system, use of classical polyester Tg elevating monomers such as diallyl isophthalate (DAIP), triallyl cyanurate (TAC) and triallyl isocyanurate (TAIC) with Derakane type vinyl esters were investigated. DEN 438 and methacrylic acid were reacted

together in DAIP, TAIC and TAC respectively to give resins containing 75 percent by weight vinyl ester and 25 percent by weight reactive monomer. The attempted vinyl ester resin preparation in TAC gelled and was discarded.

The two successful preparations were cured, cut into 1/4 inch cubes and characterized for wet and dry DTUL behavior. These results are given in Table 9. Twenty-four hour water boiled DTUL's were all between 142°C and 150°C and moisture weight gains ranged between 2.2 and 3.2 percent. The DAIP comonomer appears favored based on its lower moisture weight gain values and lack of cracking on redry. This was the first and only vinyl ester cube which did not crack after water boil and subsequent redry.

Char yields were lowered as expected with use of the reactive comonomers but increased slightly more than 10 percentage points with the AA 406 additive.

Based on the 24 hour water boiled DTUL's of the methacrylic acid/DEN 438/DAIP system, it was selected for further characterization efforts. To increase the viscosity of the system DEN 439 was investigated briefly. DEN 439 and methacrylic acid were reacted together with 25 percent DAIP to give a more viscous system which provided more acceptable prepreg drape and tack properties. Char yield benefit of a phosphorus additive was briefly investigated with addition of 2 phr triallyl phosphite to the DEN 439-methacrylate/DAIP system. Results of the moisture resistance and char yield tests are given in Table 10 for the DEN 439-methacrylate/DAIP system with and without the phosphorus additive.

The DEN 439-methacrylate/DAIP system was selected for composite characterization efforts. An idealized structure of this system is provided in Table 10.

TABLE 9. MOISTURE RESISTANCE AND CHAR YIELD TESTING OF METHACRYLIC ACID/DEN 438/TAIC AND DAIP RESINS[a]

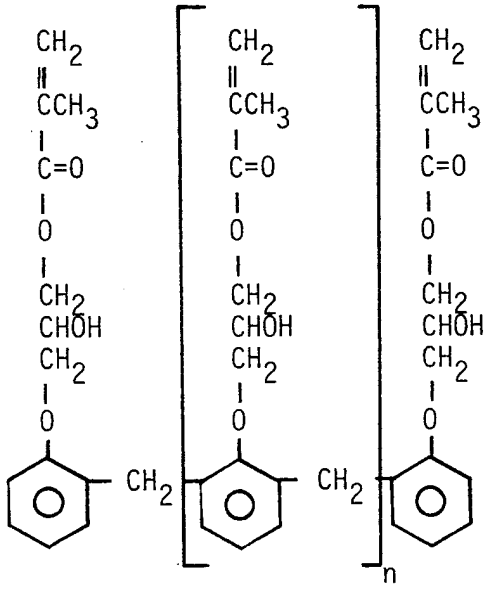
Code	Polymers and Additives	DTUL, °C @ 3.1 MPa (449 psi)[b] and 15°C/minute Heating Rate			Weight Change with Water Boil and Redry			Y_c[d] (Percent)
		Initial	24 Hr Water Boil	Δ Tg	Percent Weight Gain Water Boil	% Wt Gain After Redry 1 Hr @ 220°C	Cracks in Sample After Redry	
C-55	DEN 438 - Methacrylate with 25 percent by weight diallyl isophthalate	(182)	(150)	-32	2.22	-0.06	No	18
C-55P	C-55 Post cured for three hours at 216°C	(168)	(145)	-23	2.35	-0.38	No	
C-56	DEN 438 - Methacrylate with 25 percent by weight diallyl isophthalate and 5 phr AA 406	132, (178)	130, (150)	-2, -28	2.42	-1.17	Yes	30
C-56P	C-56 Post cured for three hours at 216°C	(165)	(150)	-15	3.23	-0.85	Yes	
C-57	DEN 438 - Methacrylate with 25 percent by weight triallyl isocyanurate	120, (153)	(142)	22, -11	3.24	-0.31	Yes[c]	17
C-57P	C-57 Post cured for three hours at 216°C	(143)	(143)	0	3.17	-0.31	Yes	
C-58	DEN 438 - Methacrylate with 25 percent by weight triallyl isocyanurate and 5 phr AA 406	110, (155)	(145)	35, -10	3.15	-0.79	Yes[c]	28
C-58P	C-58 Post cured for three hours at 216°C	(162)	(150)	-12	3.20	-0.50	Yes	

[a] Catalyzed with 0.5 phr t-butylperbenzoate and 1.5 phr Lupersol 101, then gelled at 75°C and cured through four hours at 175°C
[b] Parenthesis indicate expansion Tg without penetration
[c] Sample cracked during the wet DTUL test at 180°C
[d] Char yield at 800°C in N_2 (0.2 liter/minute) at a heating rate of 15°C/minute; sample through 60 mesh

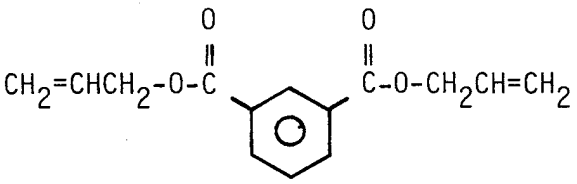
TABLE 10. MOISTURE RESISTANCE AND CHAR YIELD CHARACTERIZATION OF DEN-439/METHACRYLATE/DAIP RESIN SYSTEM

Code	Polymers and Additives[a,b]	DTUL, dry[c]	DTUL 24 Hr. Water Boil	% Water Absorbed 24 Hr Water Boil	Char Yield[d]
C-59	DEN 439-methacrylate and 25 Percent Weight DAIP	(150), (185)	(143)	- 3.29	17%
C-60	C-59 plus 2 phr triallyl phosphite	(160)	(150)	3.14	24%

[a]Catalyzed with 0.5 phr t-butylperbenzoate and 1.5 phr Lupersol 130
[b]Cure schedule: room temperature to 75°C, then 75°C to 175°C at ¼°C/minute and held at 175°C for 2 hours
[c]Parenthesis indicate expansion Tg without penetration
[d]Char yield at 800°C in N_2 (0.2 liter/minute) at a heating rate of 15°C/minute; sample through 60 mesh



DEN 439-methacrylate



DAIP

3.5 Initial Composite Evaluations

Resin compositions selected for evaluation in graphite composites were based principally on moisture resistance test results of neat resin cubes. The three resin compositions selected are listed below. Fabrication procedures are given in the experimental section of the report.

- 4,4'-DCTMDM
- 4,4'-DCTMDM/Novolac cyanate (50/50)
- DEN 439 with methacrylic acid in DAIP

Table 11 provides flexural and short beam shear strengths of the cyanate resin/Thornel 300 graphite composites investigated. Laminates DD33-128 and DD33-129 were prepared from 4,4'-DCTMDM monomer without recrystallization. Laminate No. DD33-128 was prepared from fabric* as received from the vendor and Laminate No. DD33-129 was prepared from this fabric with the epoxy size removed from the carbon fiber by MEK extraction. Due to the difference in resin content between the two composites the two laminates are not strictly comparable. However, the percentage short beam shear strength retentions (before and after water boil) seem to indicate that removal of the Thornel 300 size was beneficial to moisture resistance. The DD33-128 laminate retained 63 percent of its original 121°C (250°F) short beam shear strength after 24 hour water boil and the DD33-129 laminate retained 71 percent of its original 121°C (250°F) short beam shear strength after 24 hour water boil.

Both laminates showed thermo-plasticity at 177°C (350°F) in short beam shear testing after 24 hour water boil. It was concluded that the 24 hour water boil DTUL of 198°C obtained on the resin casting which accompanied the composite was insufficient for good performance at

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*95 Percent unidirectional/5 percent Dacron from Textile Products

TABLE 11. MOISTURE RESISTANCE OF THORNEL 300/CYANATE[a] COMPOSITES

Laminate Number	Resin Content, %	Specimen Conditioning	Flexural Strength, MPa (Ksi)/ Modulus, GPa (Msi)			Short Beam Shear Strength MPa (Ksi)		
			Test Temperature			Test Temperature		
			Ambient	121°C(250°F)	177°C(350°F)	Ambient	121°C(250°F)	177°C(350°F)
4,4'-DCTMDM[a]								
DD33-128	43	Initial, dry	1255(182)/ 79.3(11.5)		165(24)/ 13.8(2.0)[b]	92.3(13.1)	52.0(7.45)	b
		24 Hr water boil				51.0(7.40)	32.3(4.69)	b
		500 Hr, 120°F, 95+% RH				82.0(11.9)	36.4(5.28)	b
DD33-129	34	Initial, dry	1558(226)/ 103(14.9)		869(126)/ 96.5(14.0)	88.2(12.8)	63.2(9.17)	43.4(6.29)
		24 Hr water boil				66.9(9.71)	44.8(6.51)	b
		500 Hr, 120°F, 95+% RH				83.4(12.1)	51.4(7.46)	b
DD33-133	37	Initial, dry	1158(168)/ 92.3(13.4)		813(118)/ 90.3(13.1)	88.2(12.8)	67.6(9.80)	49.6(7.20)
		24 Hr water boil	1165(169)/ 90.3(13.1)		670(97.2)/ 93.0(13.5)	76.5(11.1)	54.9(7.96)	40.5(5.87)
NOVOLAC CYANATE								
DD44-28	35	Initial, dry	1089(158) 80.6(11.7)		1027(149) 82.7(12.0)	82.7(12.0)	75.1(10.9)	65.6(9.52)
		24 Hr water boil	1358(197) 93.8(13.6)		779(113) 85.4(12.4)	76.5(11.1)	54.1(7.85)	40.7(5.90)
4,4'-DCTMDM/NOVOLAC CYANATE (50/50)								
DD33-138	37	Initial, dry	1413(205)/ 79.2(11.5)		986(143)/ 91.0(13.2)	108(15.7)		66.9(9.72)
		24 Hr water boil	1254(182)/ 100(14.5)		813(118)/ 88.9(12.9)	101(14.7)		40.6(5.89)

[a] 4,4'-DCTMDM = 4,4'-dicyanato-3,3',5,5'-tetramethyldiphenylmethane
[b] = thermoplastic failure

177°C (350°F). Fiber surface treatment may also be implicated in wet strength retention. As described in Reference 9, a dry DTUL of about 228°C is suggested as a minimum starting place to achieve state-of-the-art performance for 177°C (350°F) performing resins.

Consequently, the "as prepared" resin system was recrystallized from a hexane:cyclohexane (3:1) mixture to obtain 80 percent yield of purer dicyanate monomer with a melting point of 106°-to-107.5°C. Properties of the neat resin casting which accompanied preparation of the Thornel 300 composite are given in Table 12. The catalyzed* crystallized monomer resin system was cured for six hours at 218°C (425°F) even though infrared spectral analysis of the as prepared resin system showed complete loss of cyanate absorption after its one hour at 204°C (400°F) cure, it is possible that the 218°C cure may have been responsible for the higher DTUL obtained.

Laminate No. DD33-133 (100 percent unidirectional) was prepared from the recrystallized 4,4'-DCTMDM and cured for six hours at 218°C (425°F). The percentage of 177°C (350°F) short beam shear strength retention after 24 hour water boil was 82 percent which is excellent. The dry strength however was not as high as state-of-the-art or the 100 percent novolac cyanate given in Table 11 as DD44-28.

500 Hour (21 day), 120°F, 95+ percent RH aging condition gives better composite property retention than the 24 hour water boil condition as seen with Laminates DD33-128 and DD33-129.

The development of a cyanate resin system with the initial dry elevated temperature composite strength retention of the novolac cyanate

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*Zinc stearate catalyst system (see Table 5; catalyst B).

TABLE 12. DTUL COMPARISON OF NEAT RESIN CASTINGS OF THE 4,4'-DCTMDM RESIN SYSTEM

4,4'-DCTMDM Resin Casting Cured with Laminate	DTUL, dry	DTUL, 24 Hr. Water Boil	% Water Sorbed 24 Hr. Water Boil	Char Yield[c]
As prepared[a]	205 onset	190 onset		
	208 extrapolated	198 extrapolated	1.35	34
Recrystallized[b]	240 onset	235 onset		
	252 extrapolated	237 extrapolated	1.32	35

[a]Heated until gelled at 125°C, then one hour at 204°C
[b]Heated two hours at 125°C; one hour at 135°C; one hour at 145°C (gelled); overnight at 144°C; six hours at 216°C
[c]Char yield at 800°C in N_2 (0.2 liter/minute) at a heating rate of 15°C/minute; sample through 60 mesh

resin and the moisture resistance of the 4,4'-DCTMDM resin was attempted by blending the two systems. The composite from this 50/50 blend is given in the table as Laminate No. DD33-138. The room and elevated temperature shear strengths are superior to the unblended 4,4'-DCTMDM composites. The strengths compare favorably with the strengths of the unmodified novolac cyanate system at 177°C (350°F). The superiority of the blend however to provide higher wet strengths was not demonstrated in either short beam shear in flexural tests as seen in the table. The wet and dry 177°C (350°F) short beam shear properties of the three resin systems are as follows {MPa (ksi)}:

	Dry	After 24 Hour Water Boil	Strength Retention, Percent
4,4'-DCTMDM	49.6 (7.20)	40.5 (5.87)	82
50/50 4,4'-DCTMDM/novolac	66.9 (9.72)	40.6 (5.89)	61
Novolac cyanate	65.6 (9.52)	40.7 (5.90)	60

Thus, even though the percentage of strength retention of the first system is superior and the blend has improved initial dry strengths, all three systems have essentially the same final strength even though the percentage of moisture weight gains after 24 hour water boil on the neat resin cubes were 1.3, 1.9 and 4.6 respectively (top-to-bottom). The final "wet" DTULs were 240°C, 225°C, and 220°C, respectively.

Consequently, even though all three systems appear to maintain approximately the same 177°C (350°F) strength levels after 24 hour water boil, moisture aging for long periods at e.g., 120°F should show differences between the systems. The 4,4'-DCTMDM and 50/50 4,4'-DCTMDM/novolac cyanate were selected for this study which was conducted in the final composite evaluation efforts are described in Section 3.5.

The short beam shear and flexural properties of the DEN 439-methacrylate/DAIP unidirectional Thornel 300 graphite composite are given in

Tables 13 and 14, respectively. Even though the short beam shear properties are approximately equivalent to those obtained with the Derakane 470-36 (styrene removed)/Thornel 300 composite previously reported (Reference 3), the flexural properties are superior to the Derakane 470-36/Thornel 300 system. Composite use at 177°C (350°F) is questionable, however at least a 121°C (250°F) use temperature appears probable. A 72 percent short beam shear strength retention at 121°C (250°F) was obtained after 24 hour water boil.

The DEN 439-methacrylate/DAIP system was selected for final composite evaluation efforts described in Section 3.6.

TABLE 13. SHORT BEAM SHEAR PROPERTIES OF DEN 439/ METHACRYLATE/DAIP GRAPHITE COMPOSITES

Laminate No.	Specimen Conditioning	Short Beam Shear Strength, MPa (psi) Test Temperature		
		Ambient	121°C (250°F)	177°C (350°F)
DD 33-135	Initial, dry	95.1 (13.8)	48.9 (7.1)	33.9 (4.9)
DD 33-135	24 Hour water boil		35.2 (5.1)	

TABLE 14. FLEXURAL PROPERTIES OF DEN 439/ METHACRYLATE/DAIP GRAPHITE COMPOSITES

Laminate No.	Specimen Conditioning	Flexural Strength, MPa (Ksi)/Modulus, GPa (Msi) Test Temperature		
		Ambient	121°C (250°F)	177°C (350°F)
DD 33-135	Initial, dry	1585 (230)/ 110 (16.0)	1027 (149)/ 94.4 (13.7)	669 (97)/ 97.2 (14.1)

3.6 Final Composite Evaluation

Only two resin systems were originally planned to be evaluated in this portion of the program. The DEN 439 reacted with methacrylic acid in diallyl isophthalate (DAIP) was selected. Selection of a cyanate resin candidate based on moisture resistance tests however was not conclusive. Consequently, both the 4,4'-DCTMDM and the 50/50 blend of 4,4'-DCTMDM and novolac cyanate were selected for evaluation in large composites to further evaluate the moisture resistance of these two systems.

Thirteen (13) 20.3 cm X 20.3 cm (8" X 8") unidirectional Thornel 300 composites were prepared. The physical properties of the laminates are given in Table 15. Low void contents were obtained in nearly all of the composites however, fiber volumes were not controlled as well as desired.

The first two DEN 439/methacrylate/DAIP composites cracked when processed through the entire cure schedule. Consequently, the last five composites from this resin system were removed hot from the trap mold after one hour cure at 110^{o}C and post cure occurred as a secondary operation under nitrogen. Typical successful composite fabrication procedures are given in the experimental section of this report.

The low fiber volume (45.4 percent) DEN-439/methacrylate/DAIP composite (DD33-137) was the result of late pressure application (after gel) and resulted in applying pressure to the remainder of the DEN-439/methacrylate/DAIP layups upon placing them in the press. The low fiber volume (47.1 percent) 4,4'-DCTMDM composite was the result of a runaway top platen temperature and gel prior to pressure application.

Laminate Numbers 33-139A, 33-141E, C and D were selected for mechanical test characterization due to their fiber volumes being nearly the same and their zero void contents.

TABLE 15. PHYSICAL PROPERTIES OF THORNEL 300 UNIDIRECTIONAL COMPOSITES USING THE SELECTED RESIN SYSTEMS

Laminate Number	Polymers	Resin Content, Weight Percent	Specific Gravity, g/cc	Fiber Content, Volume Percent	Calculated Void Content, Volume Percent
33-137*	DEN 439/methacrylate/DAIP	46.6	1.48	45.4	0
33-139A*	↓	33.2	1.56	59.3	0
33-139B	↓	27.7	1.53	65.4	2.5
33-140C	↓	27.1	1.57	66.1	1.3
33-140D	↓	31.6	1.54	61.1	1.3
33-141E	↓	32.6	1.54	58.5	0
33-141F	↓	28.1	1.56	64.9	0.6
A	Novolac cyanate/4,4'-DCTMDM 50/50	36.0	1.50	54.6	0
B	↓	37.7	1.50	52.2	0
C	↓	30.3	1.53	60.8	0
D	4,4'-DCTMDM	29.8	1.52	60.5	0
E	↓	29.9	1.51	60.9	0.4
F	↓	42.2	1.35	47.1	4.4

*Cracked from cure shrinkage

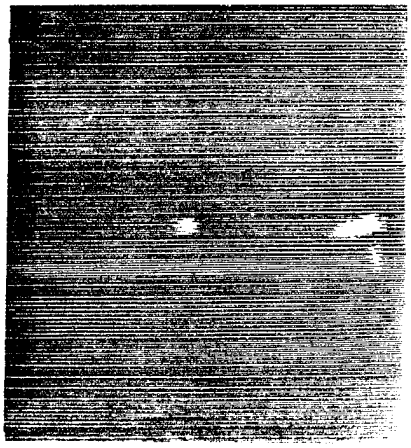
C-scan was conducted on the "uncracked" composites. C-scans of the DEN 439/methacrylate/DAIP composites are given in Figure 1 and of the cyanate resins in Figure 2. In most cases, high quality composites were obtained. Occasional non-bond areas are seen in some of the laminates, and the laminate (F; 4,4'-DCTMDM) to which pressure application was tardy, gave the poor C-scan seen in Figure 2.

Initial dry flexural properties of the composites are given in Table 16. Properties after heat and humidity aging are also provided. Short beam shear properties of the composites are given in Table 17.

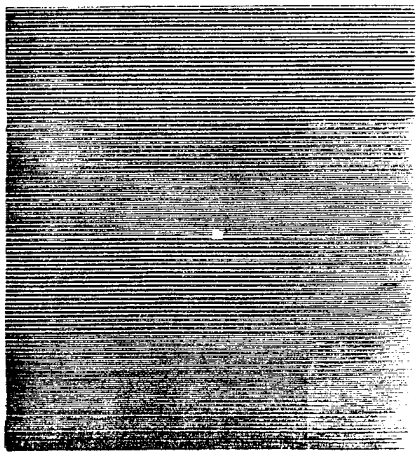
The initial, dry flexural and short beam shear strengths of the 50/50 novolac cyanate/4,4'-DCTMDM composites are essentially equivalent to state-of-the-art 177°C (350°F) performing composite systems. Elevated temperature short beam shear strength 177°C (350°F) is 59 percent of the room temperature strength compared to 60 percent in Thornel 300/5208 composites. This slight short fall may be due to the uncured epoxy resin in the composite from the fiber size. Typically one-to-two percent by weight fiber size is used and this may amount to nearly five percent by weight "plasticizer" in the composite resin matrix.

The 4,4'-DCTMDM composites showed good flexural and short beam shear strengths at room temperature but only modest strengths at 121°C (250°F) and were thermoplastic at 177°C (350°F). Expansion curves were conducted in the composite and the neat resin cube which accompanied the composite through cure. The Tg of the neat resin cube was 222°C (432°F) and of the composite was 177°C (350°F). Since the prepreg was prepared by hot melt techniques, the only readily apparent contaminate is the epoxy fiber size. As to whether the resin was plasticized by the epoxy or the cyanate cure chemistry altered is not clear. Further experimentation will be required to clarify this point.

The DEN 439/methacrylate/DAIP composites showed improved elevated temperature strengths over the small composite previously discussed but



DD33-139B



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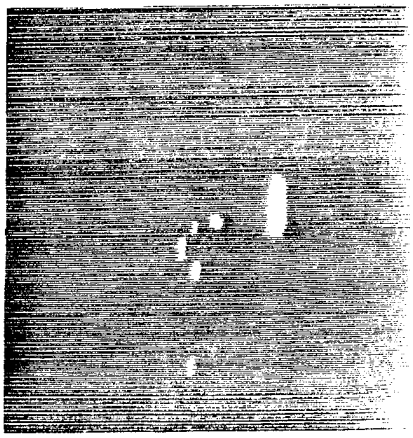
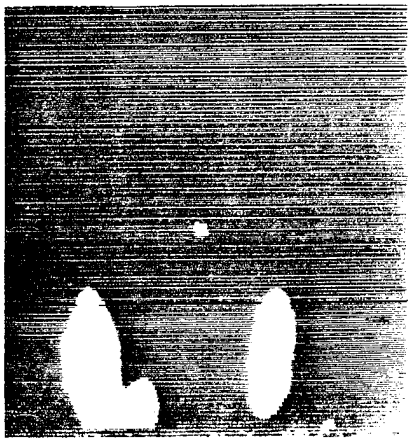
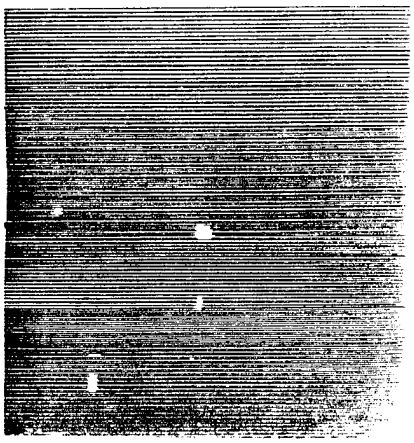


DD33-140D



DD33-141E

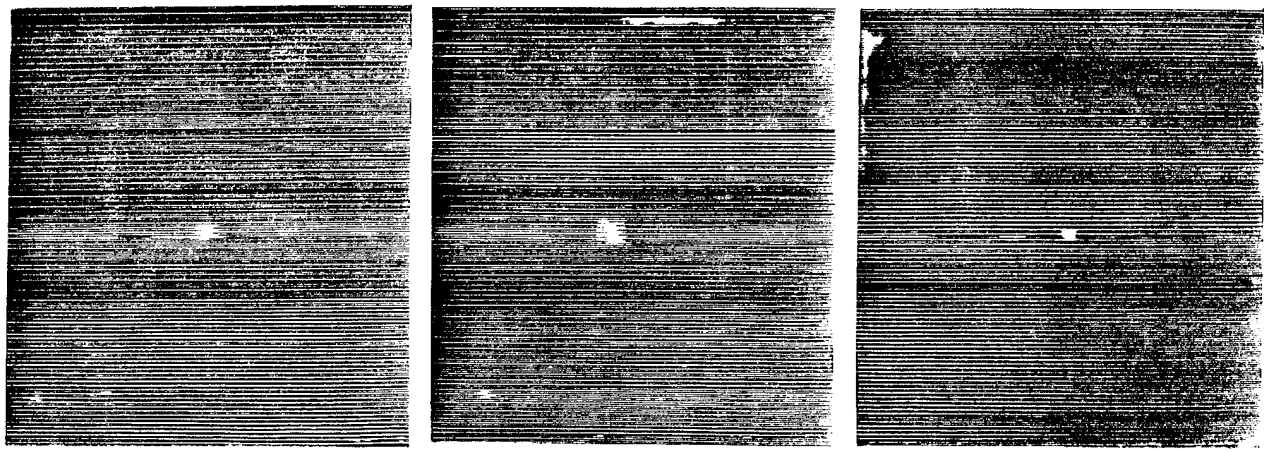


DD33-141F

NOTES:

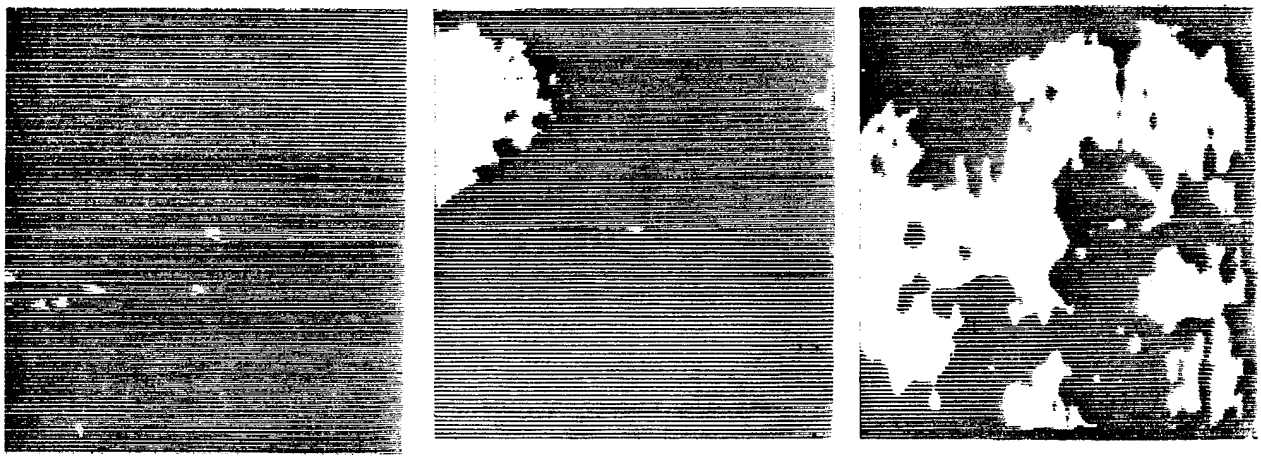
1. White areas in center of composites are lead references.
2. Fiber direction is perpendicular to scan line.
3. See Table 15 for laminate codes.

Figure 1. C-scans of uncracked DEN 439/methacrylate/DAIP unidirectional graphite composites



A B C

50/50 Novolac Cyanate/4,4'-DCTMDM Composites



D E F

4,4'-DCTMDM Composites

NOTES:

1. White areas in center of composites are lead references.
2. Fiber direction is perpendicular to scan lines.
3. See Table 15 for laminate codes.

Figure 2. C-scans of cyanate unidirectional graphite composites.

TABLE 16. FLEXURAL PROPERTIES OF CYANATE AND DEN 439/METHACRYLATE/DAIP UNIDIRECTIONAL GRAPHITE COMPOSITES

Laminate Number	Specimen Conditioning	Flexural Strength, MPa (Ksi)/Modulus GPa (Msi)[a] Test Temperature, °C (°F)			Comments
		Ambient	121°C (250°F)	177°C (350°F)	
DEN-439/METHACRYLATE/DAIP					
DD33-139A	Initial, dry	1510(219)/ 83.4(12.1)	1013(147)/ 91.7(13.3)	765(111)/ 91.7(13.3)	--
DD33-140D	Initial, dry	1379(200)/ 96.5(11.1)	1040(151)/ 92.4(13.4)	813(118)/ 89.6(13.0)	--
DD33-140D	500 Hours, 177°C, Air	1434(208)/ 93.6(13.6)	1179(171)/ 91.0(13.2)	993(144)/ 83.4(12.1)	0.25% weight loss
DD33-140D	1000 Hours, 49°C, 95+% RH	1448(210)/ 75.1(10.9)	793(115)/ 88.9(12.9)	565(82)/ 76.5(11.1)	1.07% weight gain
DD33-139A	1000 Hours, 60°C, 95+% RH	798(168)/ 91.7(13.3)	724(105)/ 84.8(12.3)	593(86)/ 80.0(11.6)	1.20% weight gain
NOVOLAC CYANATE/4,4'-DCTMDM					
C	Initial, dry	1689(245)/ 106(15.4)	1475(214)/ 95.8(13.9)	1131(164)/ 104(15.1)	--
	500 Hours, 177°C, air	1765(256)/ 133(19.3)	1399(203)/ 116(16.8)	1124(163)/ 108(15.7)	0.16% weight loss
	1000 Hours, 49°C, 95+% RH	1282(186)/ 91.7(13.3)	1206(175)/ 10.7(15.5)	820(119)/ 95.8(13.9)	0.88% weight gain
	1000 Hours, 60°C, 95+% RH	1586(230)/ 85.4(12.4)	931(135)/ 86.2(12.5)	593(86)/ 71.7(10.4)	1.07% weight gain
4,4'-DCTMDM					
D	Initial, dry	1503(218)/ 88.2(12.8)	1144(166)/ 90.3(13.1)	648(94)/ 86.2(12.5)	--
	500 Hours, 177°C, air	1572(228)/ 141(20.4)	1172(170)/ 116(16.8)	248(36)/ 31.7(4.6)	0.09% weight loss
	1000 Hours, 49°C, 95+% RH	1310(190)/ 88.9(12.9)	958(139)/ 88.9(12.9)	352(51)/ 49.6(7.2)	0.62% weight loss
	1000 Hours, 60°C, 95+% RH	1420(206)/ 87.6(12.7)	1075(156)/ 103(15.0)	255(37)/ 26.9(3.9)	0.71% weight gain

[a]Average of two specimens at each test condition

TABLE 17. SHORT BEAM SHEAR STRENGTHS OF CYANATE AND DEN 439/METHACRYLATE/DAIP UNIDIRECTIONAL GRAPHITE COMPOSITES

Laminate Number	Specimen Conditioning	Short Beam Shear Strength MPa (KSI)[a] Test Temperature, °C (°F), Three Specimens per Test			Comments
		Ambient	121°C (250°F)	177°C (350°F)	
DEN-439/METHACRYLATE/DAIP					
DD33-140D	Initial, dry	68.2(9.9)	55.8(8.1)	49.6(7.2)	--
DD33-140D	500 Hours, 177°C air	65.5(9.5)	58.6(8.5)	48.3(7.0)	0.40% weight loss
DD33-140D	1000 Hours, 49°C, 95+% RH	61.4(8.9)	22.3(4.7)	24.8(3.6)	1.36% weight gain
DD33-140D	1000 Hours, 60°C, 95+% RH	60.0(8.7)	22.8(4.8)	24.8(3.6)	1.09% weight gain
NOVOLAC CYANATE/4,4'-DCTMDM					
C	Initial, dry	105(15.3)	80.0(11.6)	60.0(8.7)	--
	500 Hours, 177°C, air	103(15.0)	80.6(11.7)	61.3(8.9)	0.16% weight loss
	1000 Hours, 49°C, 95+% RH	90.3(13.1)	56.5(8.2)	34.5(5.0)	1.04% weight gain
	1000 Hours, 60°C, 95+% RH	93.8(13.6)	51.7(7.5)	30.3(4.4)	1.13% weight gain
4,4'-DCTMDM					
D	Initial, dry	104(15.1)	68.9(10.0)	40.0(5.8)	--
	500 Hours, 177°C, air	94.2(14.1)	57.2(8.3)	b	0.03% weight loss
	1000 Hours, 49°C, 95+% RH	88.9(12.9)	46.9(6.8)	b	0.65% weight gain
	1000 Hours, 60°C, 95+% RH	84.1(12.2)	42.1(6.1)	b	0.69% weight gain

[a]Average of three specimens at each test condition
[b]Thermoplastic failure

at some sacrifice to initial room temperature strength. The previously obtained short beam shear was 95.1 MPa (13.8 ksi) and that obtained in the larger composite 68.2 MPa (9.9 ksi). The short beam shear strength at 177°C (350°F) of 49.6 MPa (7.2 ksi) is 73 percent of the room temperature value. Infrared spectral analysis of a film of the DEN 439/methacrylate/DAIP resin cured in a similar manner to the composite showed no residual unsaturation. Thus, even though catalyst and cure studies could lead to improved properties, the systems cure shrinkage (2.5 linear percent) and moisture durability need to be addressed. The preliminary data obtained on this system to date however are very encouraging.

The 500 hour air aging of the three composite systems at 177°C (350°F) showed essentially no significant changes in the physical or mechanical properties of the systems. The flexural strength of the vinyl ester composite showed slight increases in elevated temperature strengths after aging which may be attributable to continued cure of unsaturation not detected by infrared spectral analysis. Basically, all three systems show excellent ability to withstand the 177°F (350°F) air exposure without degradation.

Moisture exposure of the three composite systems did not provide the hoped for results. Even though the 50/50 novolac cyanate/4,4'-DCTMDM composite system after moisture exposure showed strength retentions better than state-of-the-art, the composite moisture weight gains were in excess of those expected from a rule of mixture calculation. The strength retention of this cyanate system after humidity exposure is compared to diaminodiphenyl sulfone (DADS) cured MY 720 in Table 18.

Powdered resin samples (-60 mesh) were exposed to 49°C (120°F), 95+ percent relative humidity (noncondensing) until the equilibrium plateau was attained (a few days). The moisture weight gains of the powders are compared to the weight gains of the composites in Table 19.

TABLE 18. COMPARISON OF STRENGTH RETENTION AFTER HUMIDITY EXPOSURE OF CYANATE AND 5208 THORNEL 300 GRAPHITE COMPOSITES

Resin	Short Beam Shear Strength, MPa (ksi)	
	Room Temperature	177°C (350°F)
DADS/MY 720*		
Initial, dry	101 (14.7)	58.5 (8.5)
After 31 day exposure to 49°C (120°F), 95+ percent RH	85.5 (12.4)	29.6 (4.3)
Percent strength retention	(84)	(51)
50/50 Novolac cyanate/4,4'-DCTMDM		
Initial, dry	103 (15.0)	61.3 (8.9)
After 42 day exposure to 49°C (120°F), 95+ percent RH	90.3 (13.1)	34.5 (5.0)
Percent strength retention	(87)	(56)

*Data from Reference 9

TABLE 19. CALCULATED MATRIX RESIN MOISTURE WEIGHT GAINS COMPARED TO NEAT RESIN SAMPLES

Resin	Moisture Content, Percent	
	Neat Resin	Composite Resin*
DEN 439/methacrylate/DAIP	2.9	3.2 (flex specimens)
		4.1 (shear specimens)
50/50 Novolac cyanate/4,4'-DCTMDM	1.6	2.9 (flex specimens)
		3.4 (shear specimens)
4,4'-DCTMDM	1.0	2.1 (flex specimens)
		2.2 (shear specimens)

*Calculated from the weight percent resin in the composite and the moisture weight gain of the composite specimens. Assumes fibers gain essentially no weight in humid environments.

The vinyl ester composite matrix resin (calculated value) showed moisture weight gains only slightly in excess of the neat resin samples whereas both cyanate resins showed moisture weight gains which were about 100 percent in excess of the expected values. Composites must be prepared from unsized fibers and the strength retention versus moisture weight gain data repeated.

It is concluded that both the cyanate and vinyl ester resins hold promise as candidates for graphite composite matrix resins. Cyanate resins show excellent moisture resistance as well as high char yields. Even though composites with strength retentions clearly superior to state-of-the-art composites were not demonstrated on this effort, further development efforts are expected to produce such composites. Continued development of vinyl ester resins is also expected to produce composites with superior moisture resistance.

SECTION 4

CONCLUSIONS AND RECOMMENDATIONS

1. Novolac cyanate resin systems exhibited excellent moisture resistance and char yields. A 50/50 blend of the phenol-formaldehyde novolac cyanate resin with the 4,4'-dicyanato-3,3',5,5'-tetramethyldiphenylmethane (4,4'-DCTMDM) resin exhibited an anaerobic char yield of 46 percent at 800°C. Composites prepared from the resin blend and Thonel 300 graphite fiber exhibited mechanical properties equivalent to those of state-of-the-art 177°C (350°F) epoxy composites. The strength retention of the cyanate blend composites was better than that of state-of-the-art epoxy composites. However, the moisture durability potential of the cyanate system was not fully realized, possibly due to the presence of the epoxy fiber size. Further development efforts with the cyanate resin system are recommended.

2. The vinyl ester type of unsaturated polyester exhibited potential for use as a matrix for graphite composites. A 121°C (250°F) performance temperature appears to be easily within reach of such systems. Further development efforts of these systems are recommended.

3. The highly functional resorcinol formaldehyde novolac as a curative for novolac oxirane ethers or MY 720 (N,N,N',N'-tetraglycidyl methylene dianiline) produced cured compositions with very high softening temperatures. Although such systems may hold promise for high char yields, their moisture sensitivity presently offers no advantage over state-of-the-art epoxy systems.

4. Low concentrations of char promoter catalysts were effective in increasing the 800°C anaerobic char yields of novolac oxirane ethers and

unsaturated vinyl type polyesters. Novolac oxirane ethers exhibited an increase from 24-to-47 percent with a phosphorus-nitrogen (PN) additive. Vinyl esters exhibited an increase from 2-to-23 percent with the PN additive. Novolac cyanate resins exhibited only slight char yield improvement with char promoter catalysts.

SECTION 5

EXPERIMENTAL

Preparation of the Bismethacrylate of 9,9-Bis(4-glycidyloxyphenyl)fluorene

The 9,9-bis(4-glycidyloxyphenyl)fluorene starting material used had an epoxy equivalent weight (EEW) of 286.7. Its theoretical EEW is 233. Into a 250 ml polypropylene cup was placed (50g; 0.174 epoxy equivalent) powdered 9,9-bis(4-glycidyloxyphenyl)fluorene and 35g reagent grade acetone. The stirred mixture formed a fine white suspension with some dissolution of the powdered resin at room temperature. The cup was placed in a 50°C oven for 20 minutes; removed, and 1.3g Cordova AMC-2 catalyst added. Methacrylic acid inhibited with 1000 ppm hydroquinone and 250 ppm monomethoxy hydroquinone (15g; 0.174 equivalent), was added and stirred in well. The mixture was heated, with stirring, with an oil bath at 50°C. After three hours the epoxy resin was completely dissolved and the mixture's color was clear light green. The course of the reaction was followed by IR spectra and acidity titrations. The acetone was allowed to evaporate as the reaction proceeded and after heating for 20 hours at 50°C, a very viscous light green product was obtained. The acidity was determined to have changed from 0.268eq/100g of reaction mixture to 0.017eq/100g indicating essentially complete reaction. The mixture was stirred rapidly for four more hours at 50°C to allow the acetone to evaporate, after which the cup plus mixture was weighed and the product was found to contain 4g of acetone by weight. The mixture was subjected to high vacuum at 60°C for one-half hour and the weight of acetone was reduced to 3.5g or approximately four percent by weight.

Infrared spectra of the starting reaction mixture and the vinyl ester product are given in Figure 3.

Preparation of the Bis(glycidyl methacrylate) Derivative of Phthalic Anhydride

Into a 100 ml polypropylene cup was placed (19.2g; 0.135 equivalent) glycidyl methacrylate. The cup was heated in a 50°C oven for 15 minutes. Next 0.3g AMC-3 (Cordova-anhydride epoxy catalyst) was added. To this mixture phthallic anhydride (10g; 0.135 equivalent acid) was added which only partially dissolved. The mixture was heated overnight in a 35°C oven and nearly all of the anhydride dissolved. The mixture was heated further with stirring at 52°C and after two hours the anhydride was completely dissolved. The continuing reaction was followed by acidity titrations and after 24 hours at 52°C (stirring), titration provided a 0.025eq/100g acid value indicating 95 percent complete reaction.

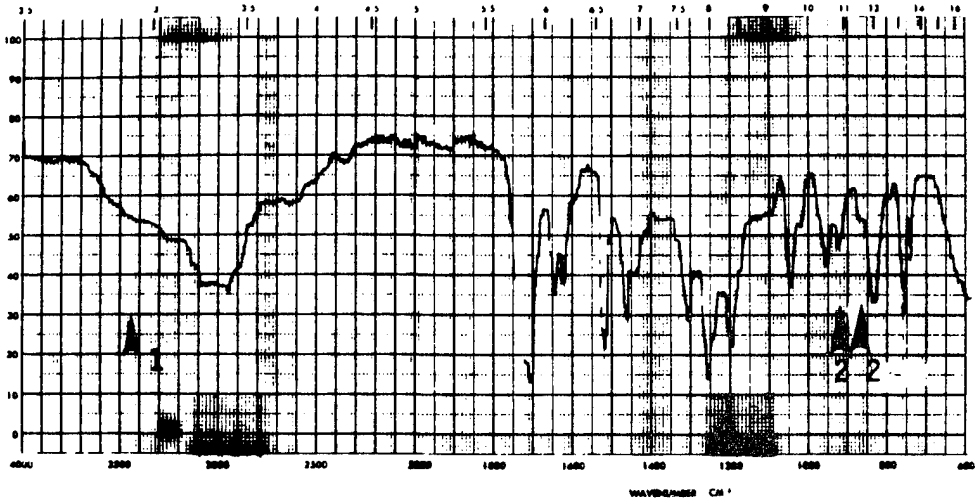
The infrared spectrum of this product is given in Figure 4.

Attempted Preparation of the Bis(glycidyl methacrylate) Derivative of 2,3-Naphthalic Acid

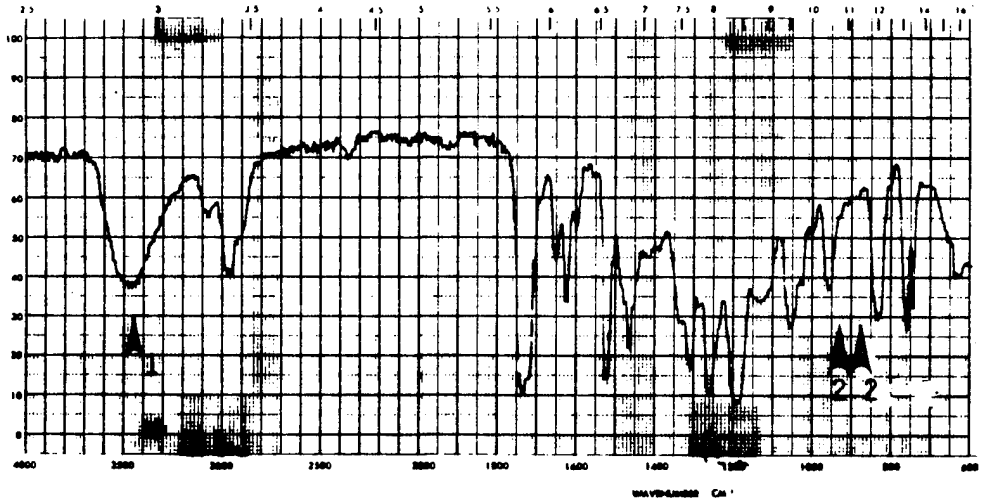
The stoichiometric mixture of 2,3-naphthalene dicarboxylic acid and glycidyl methacrylate plus AMC catalyst formed a fine suspension which did not go into solution under a variety of reaction conditions, including the addition of tetrahydrofuran as a solvent for the 2,3-naphthalic acid.

Preparation of 2,7-Diglycidyloxynaphthalene

Into a 500 ml resin pot equipped with stirrer, thermometer, and condenser were placed epichlorohydrin (231.25g; 2.5 mole) 2,7-dihydroxy naphthalene (40g; 0.25 mole) and 2 ml of water. A total of (20.5g;



Starting reaction mixture



Completed reaction

A_1 = hydroxyl
A_2 = oxirane

Figure 3. Infrared spectrum for reaction of methacrylic acid with 9,9-bis(4-glycidyloxyphenyl)fluorene

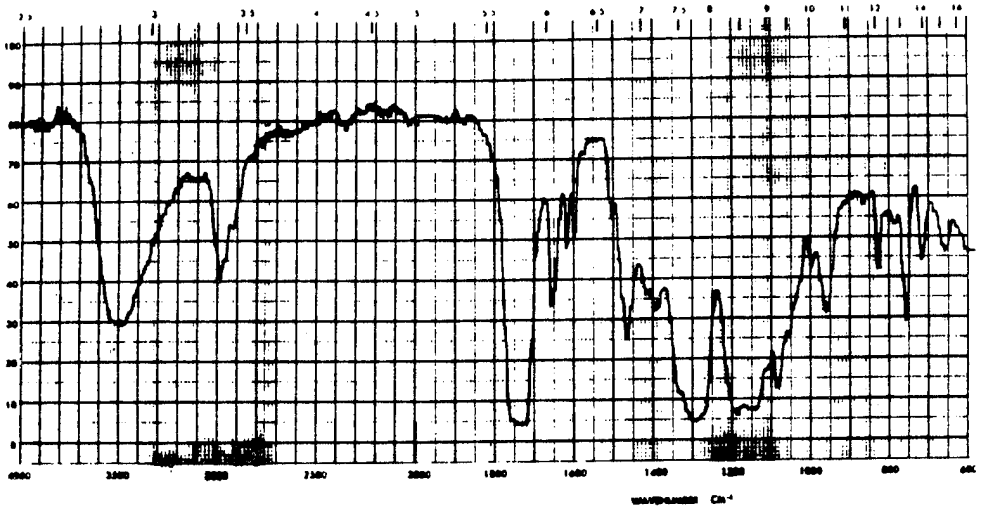


Figure 4. Infrared spectrum of reaction product of glycidyl methacrylate with phthalic anhydride.

0.513 mole) powdered sodium hydroxide was added in seven equal portions. The first portion of NaOH was added and the mixture was heated with stirring. The heating was stopped at 90°C and the heating mantle replaced by an ice water bath such that the temperature did not exceed 100°C. When the reaction temperature fell to 95°C, another portion of NaOH was added. Thus, temperature control was exercised and the remainder of the NaOH was added. After the final addition of base, no cooling was required. The mixture was transferred to a one liter single neck flask and vacuum stripped of the excess epichlorohydrin at 80°C. The viscous green product was transferred to a one liter separatory funnel with 500 milliliters of methylene chloride. The methylene chloride solution was washed three times with water. The methylene chloride layer was transferred to a one liter single neck flask and the methylene chloride removed under vacuum. Final conditions were 100°C for two hours. Upon cooling the viscosity of the product increased to that of a thick syrup. A yield of 51g obtained (75 percent of theoretical). The epoxy equivalent weight of the product was 166 (HBr method) theory is 136.

Preparation of the Bismethacrylate of 2,7-Diglycidyloxynaphthalene

In a 250 ml polypropylene beaker was placed 40g of 2,7-diglycidyloxy-naphthalene. The beaker was placed in a 50°C oven for 20 minutes. Next 1.2g AMC 2 catalyst was stirred in well and the beaker placed in the 50°C oven for 10 minutes. Methacrylic acid, 20.74g was added slowly with stirring. The viscosity went from that of a heavy oil (at room temperature) to a very low viscosity. The mixture was heated in an oil bath at 54°C. After one hour, acid titration showed 0.0856 equiv./100g of reaction mixture or a 79 percent complete reaction. After two hours titration showed 0.027 equiv./100g of reaction mixture or a 93 percent complete reaction. The reaction was allowed to proceed for another one-half hour. The product cooled to room temperature and was a spreadable paste.

Preparation of the Acrylate Ester of Resorcinol Diglycidylether (RDGE)

The epoxy equivalent weight of RDGE (Heloxy 69-Wilmington Chemical Corporation) was determined to be 120 by the HBr method.

In a 100 ml polypropylene cup was placed (30g; 0.25 equivalent epoxy) RDGE and the cup was placed in a 50°C oven for 20 minutes. Next (0.6 gm; two percent by weight epoxy) AMC-2 catalyst was hand stirred in. Then acrylic acid (18g; 0.25 equivalent) was stirred in slowly. The cup was immersed in a 50°C oil bath and true bore stirrer attached. Initial acidity titration on one gram of the mixture showed 0.518 equiv./100 gm. Theory is 0.521 equiv./100 gm. A thin film IR spectrum of the initial mixture was obtained. The mixture was allowed to react at 50°C with continuous stirring and acidity titrations were made every hour. After 5½-hours the acidity was determined to 0.0001 equiv./100g, a complete reaction. An IR spectrum was obtained. The product was low in viscosity at room temperature.

Preparation of the Methacrylate Ester of RDGE; DEN 438; and the Acrylate Ester of DEN 438

The reaction conditions for these preparations were essentially the same as in the acrylate ester of RDGE preparation described above. Methacrylic acid was used for the preparation of the methacrylate ester systems. All preparations went to completion, determined by acidity titrations and thin film IR spectra. The DEN 438 acrylate and methacrylate systems are semi-solids at room temperature.

Preparation of the DEN-439/Methacrylate/DAIP System

DEN 439 (524g; 2.62 equivalent epoxy) warmed to 70°C was thoroughly mixed with methacrylic acid (225g; 2.62 equivalent) warmed to 50°C. Next 9g AMC-2 catalyst was stirred into the mixture and 250g diallyl isophthalate was added and stirred in well. The entire mixture was transferred into a tared 2-liter resin pot equipped with true-bore stirrer, air motor, and dry air inlet/outlet. The mix was allowed to stir at room temperature and the reaction was followed by thin film IR spectra and acidity titrations. Theoretical acidity is 0.350 equiv/100g resin. The reaction was essentially complete after five days. Tertiary butylperbenzoate (2.46g; 0.25 phr) was premixed with Lupersol 130 (14.75g; 1.5 phr) and added to the mix. The catalyzed system was stored in a capped polypropylene container at 5°C to await prepregging.

Preparation of 4,4-Dihydroxy-3,3',5,5'-Tetramethyldiphenylmethane

In a 250 ml polypropylene beaker was dissolved (122.1g; 1 mole) 2,6-dimethylphenol in 122 ml glacial acetic acid. The solution was transferred into a 500 ml, 3-neck, round bottom flask equipped with

true-bore stirrer and N_2 inlet and outlet. The flask was chilled with an ice/water bath for approximately 15 minutes and 122 drops of concentrated H_2SO_4 was added. After five minutes, 43.5 ml of 37 percent formaldehyde solution (16g, CH_2O; 0.537 mole) was added over 10 minutes to the stirring solution and the ice-water bath removed upon completion of the formaldehyde addition. After 1½-hours the mix was white in color, thickening, and the flask was warm. After 3½-hours the flask was no longer warm and a stirrable, very thick, white paste was observed. The paste was büchner filtered, washed well with water, rubber dammed, and recrystallized from approximately 80:20 ethanol and water. Long, white crystals (100g; 78 percent of theory) were obtained with a melting point of 175°-to-177°C (Literature m.p. 176°).

Preparation of 2,2'-Dihydroxy-3,3',5,5'-Tetramethyldiphenylmethane

The reaction conditions and amounts were identical to the above preparation except that 2,4-dimethylphenol was used in place of 2,6-dimethylphenol. A resineous product was obtained which was difficult to recrystallize yielding 17g of white crystals, melting point 147-149°C (Literature m.p. 146°C).

Preparation of 4,4'-Dicyanato-3,3',5,5'-Tetramethyldiphenylmethane

In a 12 liter, 3-neck flask, equipped with stirrer, thermometer and addition funnel was placed (656g; 2.563 mole) 4,4'-dihydroxy-3,3',5,5'-tetramethyldiphenylmethane and 3 liters reagent acetone added. After dissolution, 1.8 liters reagent methylene chloride was added. Cyanogen bromide (600g; 5.66 mole) was dissolved into the stirring solution and the flask was immersed in an ethanol/dry ice bath. When the temperature fell to -7°C, (572g; 5.66 mole) triethylamine was added in portions maintaining the temperature of the solution between -5°C and 0°C. The reaction was allowed to continue below 0°C for 1-1/2 hours. At this time, six liters of ice water (deionized) was added to the flask and stirring continued for

twenty minutes. The water layer was aspirated off and a fresh portion of ice water (8 liters) was added and stirred with the methylene chloride solution for 20 minutes, and this process repeated to give a total of three aqueous washings. After the final water wash, most of the water layer was aspirated off and the methylene chloride layer was transferred into a six liter separatory funnel. The methylene chloride layer was drained into a four liter beaker containing 300 grams of anhydrous magnesium sulfate, stirred well, and filtered into a tared two-liter single neck distilling flask. The methylene chloride was stripped off by rotovap treatment. The product was recrystallized in a mixture of hexane/cyclohexane (3:1) and an 80 percent yield of long, wide, white crystals were obtained (m.p. 106^{o}-to-$107.5^{o}C$). Typical B-staged conditions for the product without catalyst are: 1) heat at $170^{o}C$ with stirring for 16 hours; and 2) N_2 atmosphere.

Preparation of 2,2'-Dicyanato-3,3',5,5'-Tetramethyldiphenylmethane

The cyanation of 2,2'-dihydroxy-3,3',5,5'-tetramethyldiphenylmethane was carried out under similar reaction conditions as the above cyanation reaction, varying only the amounts of the reactants and workup solvents proportionally to the starting quantity of the bisphenol. The product was recrystallized from hexane yielding small groups of clumped, white crystals with a melting point of 105.5^{o}-to-$107^{o}C$.

Thornel 300 Prepreg Preparation

Prepregs were prepared in all cases by hot melt coating a film of the resin onto Mylar, taping the coated Mylar onto a drum, overwinding the resin with Thornel 300 (24 tows per inch) and completion of the impregnation step on a hot table with a squeegee. Resin contents of the prepregs varied from 45-to-50 percent by weight.

Typical Preparation of DEN 439/Methacrylate/DAIP Unidirectional Graphite Composites

Fourteen plies of prepreg were layed into a steel trap mold with TX-1040 (Teflon/glass cloth separator) on both sides of the stack of DEN-439/methacrylate/DAIP graphite prepreg. One ply of 120 E-glass and two plies of 7781 glass fabric were placed on each side of the TX-1040 sheets as bleeders. The layup was placed in a press preheated to 104°C (220°F) and accumulator pressure {$\sim$0.17 N/m^2 (25 psi)} used to close the press to 0.25 cm (0.10 inch) thick shims. The resin gelled during heatup in approximately 10 minutes and the laminate thermocouple showed a temperature of 100°C. The laminate was cured for one hour and removed hot. After fabrication of several laminates by this procedure, several cured laminates were post cured together in a press, each separated by a ply of 7781 glass fabric under contact pressure supplied by an accumulator to prevent warpage. Post cure was a 2.5 hour heatup from 100°C-to-175°C and a one hour hold at 175°C under nitrogen.

Typical Preparation of Cyanate Resin Unidirectional Graphite Composites

Fourteen plies of prepreg were layed into a steel trap mold with TX 1040 on both sides of the stack of cyanate resin graphite prepreg. Two plies of 120 glass fabric were placed on each side of the TX 1040 sheets. The layup was placed in a press preheated to 110°C (230°F). The gel-thickening properties were noted with time and increasing temperature. Twenty-five minutes after start, 0.7 MPa (100 psi) was applied (100°C). The laminate was held at 110°C for one hour and the temperature raised to 144°C and held there for 24 hours. The temperature was increased to 218°C (425°F) and held at that temperature for four hours. It was cooled under pressure.

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APPENDIX A

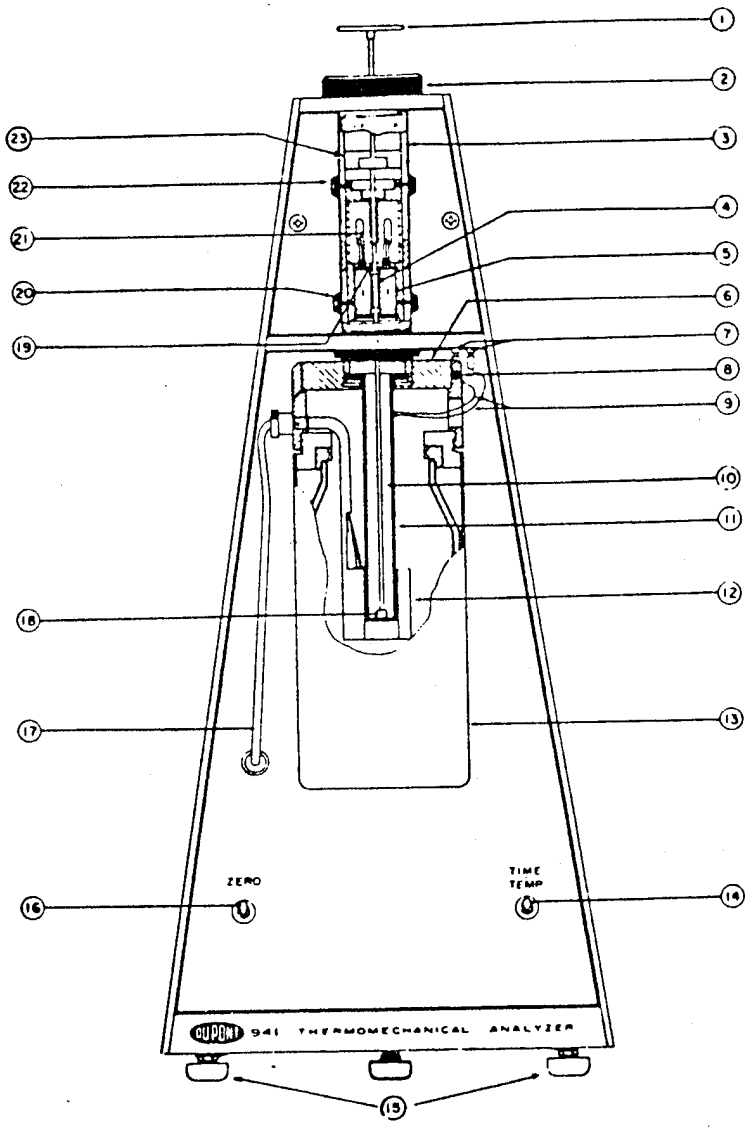
DISTORTION TEMPERATURE UNDER LOAD

Distortion temperature under load (DTUL) is carried out on a cured sample of resin with essentially parallel faces as sketched in Figure A-1. The intercept of the expansion curve with the softening curve or a change in slope of the expansion curve is taken as the temperature at which the sample will no longer support the compressive load placed upon it.

Figure A-2 shows the epoxy-novolac, DEN 438 cured with several curing agents and how DTULs relate to the target performance temperature. In the case shown, 177^{o}C (350^{o}F) is the target performance temperature and 227^{o}C is the suggested minimum DTUL to be obtained on the experimental resin system to match state-of-the-art/177^{o}C (350^{o}F) performing epoxy resin systems. See Reference 10.

FIGURE A-1

SKETCH OF SET-UP TO DETERMINE DISTORTION TEMPERATURE UNDER LOAD (DTUL)



Item	Description
1	Weight tray
2	Retainer nut
3	Head assembly
4	LVDT core
5	LVDT
6	Dewar cap
7	Thermocouple connectors
8	Set screws
9	Thermocouple wires
10	Shaft assembly (lower)
11	Sample holder tube

Item	Description
12	Heater assembly
13	Dewar
14	Time-Temp. switch
15	Adjustable legs
16	Zero switch
17	Heater lead wire
18	Sample
19	Shaft assembly (upper)
20	Transducer Position control
21	Zero spring
22	Probe Position control
23	Upper Bearing guide

DTUL experiments are conducted using a 0.025 inch diameter probe and a 100g weight on the weight tray. This places a 449 psi load on the sample.

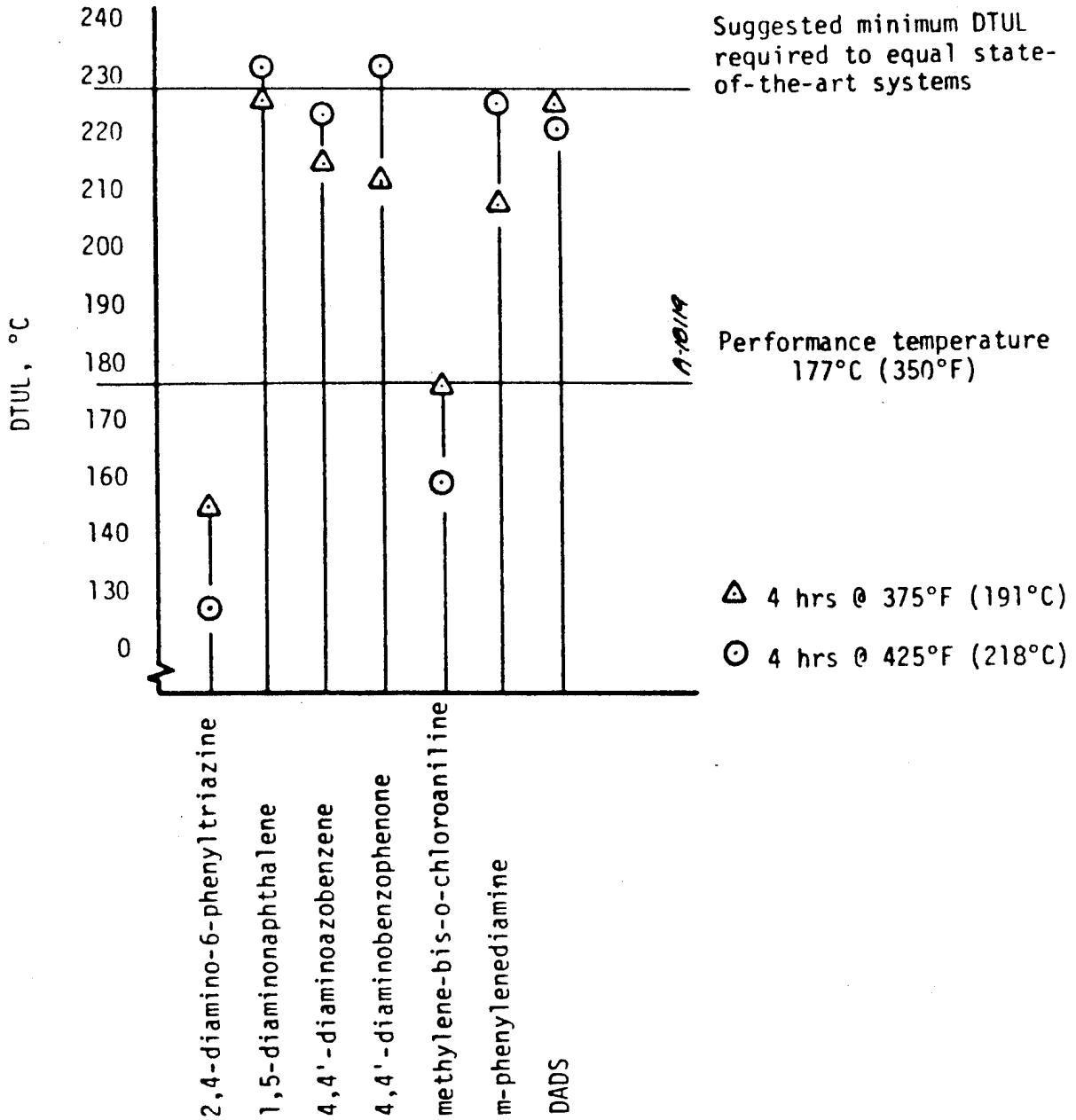


Figure A-2. Distortion temperature under loads for various curing agents with DEN 438, at two final cure temperatures.

APPENDIX B

TESORO'S CLASSIFICATION OF FLAME-RETARDANTS (REFERENCE 6)

Flame-retardant compounds of value have been identified or discovered primarily by trial and error, rather than on the basis of fundamental investigations of mechanism, or of systematic studies relating the parameters of molecular structure of flame-retardant effectiveness. The technology of flame-retardant compounds and flame-resistant polymeric materials is well advanced, while scientific principles of flame retardant classification are lacking. Known flame-retardant compounds may be grouped as follows:

1. Inorganic acids and acid-forming salts (e.g., ammonium salts of sulfuric, sulfamic, phosphoric, hydrochloric, hydrobromic, and boric acid), which act as dehydrating agents. These are solid-phase retardants, of importance where durability to leaching or washing is not required (e.g., wood, textile cellulose, and paper).

2. Inorganic salts which contribute to the formation of glassy coatings around the decomposing polymer mass (e.g., borates, phosphates, and silicates).

3. Inorganic salts and hydrates which decompose endothermically, releasing a noncombustible diluent (e.g., water) into the gas phase (e.g., hydrate alumina ($Al_2O_3 \cdot 3H_2O$), of importance in specific applications of thermo-plastic resins (e.g., carpet backings).

4. Antimony compounds, which interact synergistically with halogen-containing flame-retardants. The most important, antimony trioxide (Sb_4O_6) is extensively used in plastics and in fibers to reduce the amount of halogen-containing retardant needed, and thus minimize the effects of the modification on performance properties.

5. Organic compounds of phosphorus—generally solid-phase retardants--which are important for cellulose polymers and polyurethane polymers. The organic moiety in these flame-retardant compounds contributes compatibility and/or reactivity with the substrate, while flame-retardant effectiveness and efficiency generally depend on the phosphorus content.

6. Organic compounds of halogen—generally gas-phase retardants—important for hydrocarbon polymers and others. Effectiveness and efficiency depend on the specific halogen (Cl vs. Br), on the halogen content, on the temperature at which dehydrohalogenation of the compound occurs (thermal stability of the halogen compound, aliphatic vs. aromatic halogen) in relation to the temperature of decomposition of the polymer substrate, and on the presence of synergists (e.g., antimony).

7. Organic compounds containing both phosphorus and halogen.

8. Organic compounds containing both phosphorus and nitrogen*.

9. Miscellaneous compounds which reportedly have shown effectiveness in specific substrate polymers under some conditions of measurement (e.g., tin, titanium, and chromium compounds (wool); molybdenum salts; zinc and magnesium chlorides (wood); and thiourea and ammonium thiocyanate (nylon).

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*This class added to Tesoro's classification by Acurex.

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